

Pacific Northwest National Laboratory

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TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank 241-C-204: Results from Samples Collected on 07/02/96

B. L. Thomas
J. C. Evans
K. H. Pool

K. B. Olsen
J. S. Fruchter
K. L. Silvers

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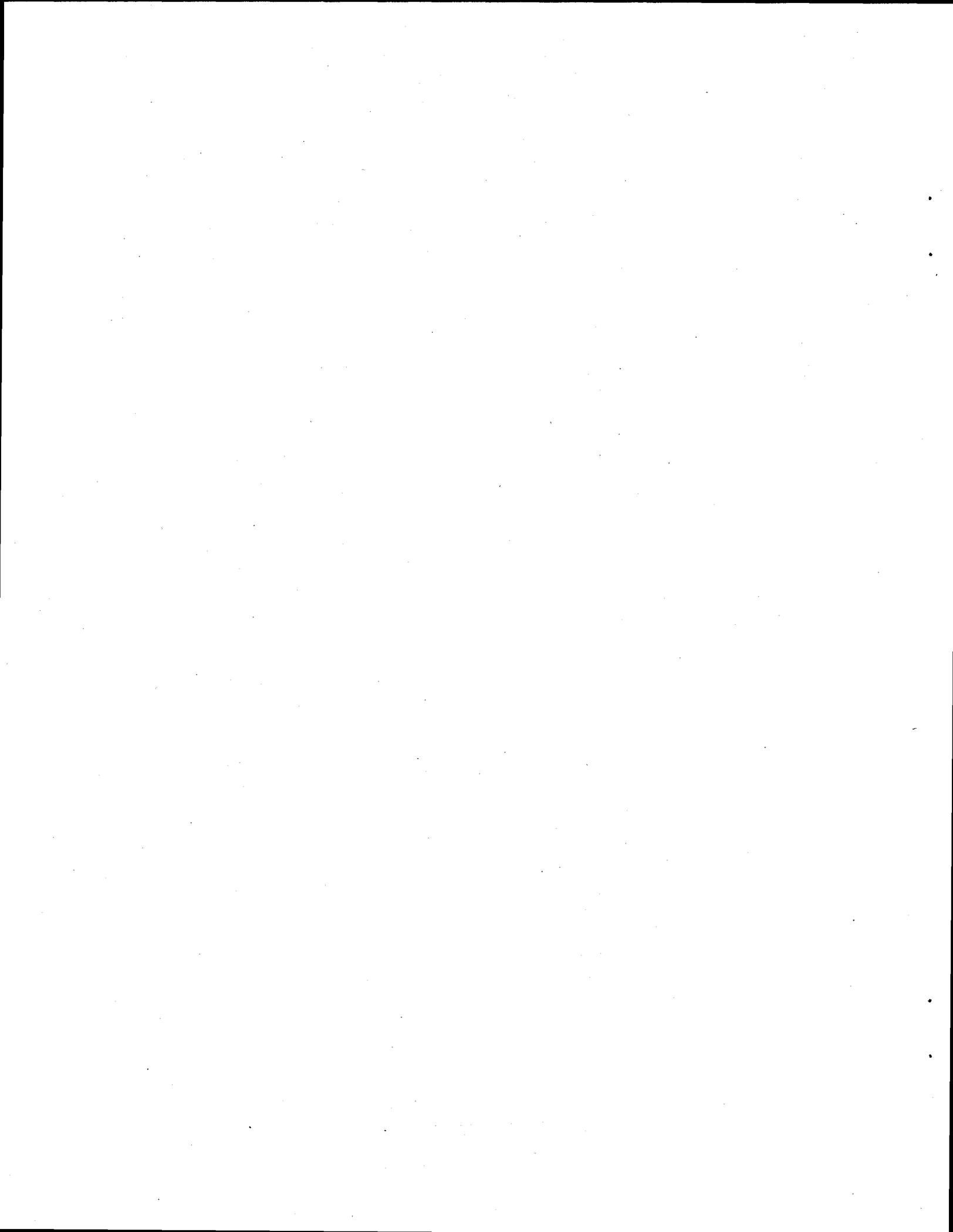
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Pacific Northwest National Laboratory
Richland, Washington 99352

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Summary

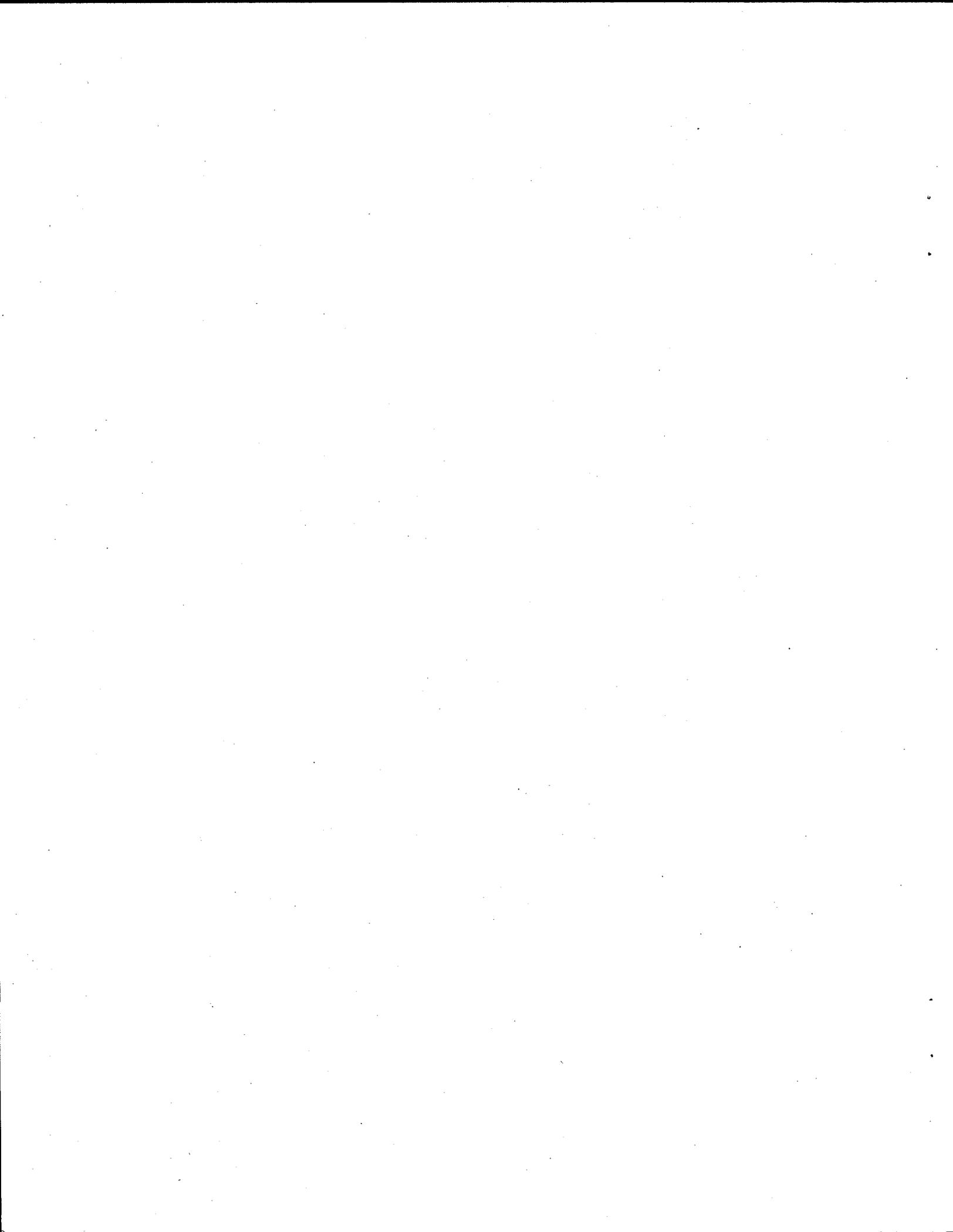
This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-C-204 (Tank C-204) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support safety 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 C-204 on 7/2/96

<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	≤ 0.84	ppmv
		NO ₂	< 0.16	ppmv
		NO	0.8 ± 0.1	ppmv
		H ₂ O	7.9 ± 0.3	mg/L
Permanent Gases	SUMMA™ Canister	H ₂	< 17	ppmv
		CH ₄	< 25	ppmv
		CO ₂	443	ppmv
		CO	< 17	ppmv
		N ₂ O	< 17	ppmv
Total Non-Methane Organic Compounds (TO-12)	SUMMA™ Canister	Non-Methane Organic Compounds	80.24	mg/m ³
Organics (TO-14)	SUMMA™ Canister	Dodecane	1.559	ppmv
		Butanal (TIC)	1.219	ppmv
		Tridecane	1.132	ppmv
Organics (PNL-TVP-10)	Sorbent Traps	1-Butanol	0.561	ppmv
		Dodecane	0.342	ppmv
		Tridecane	0.283	ppmv

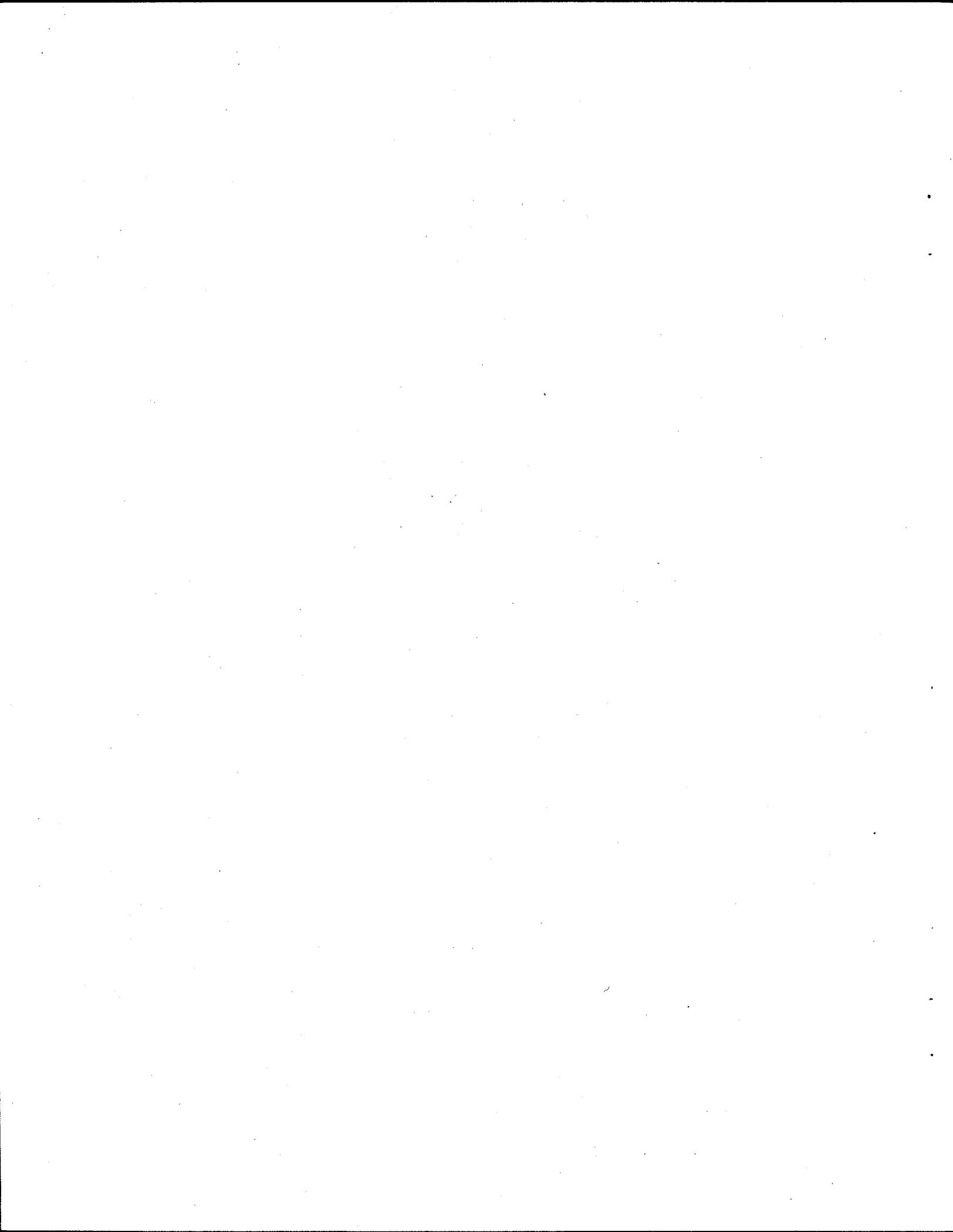
(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data.

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



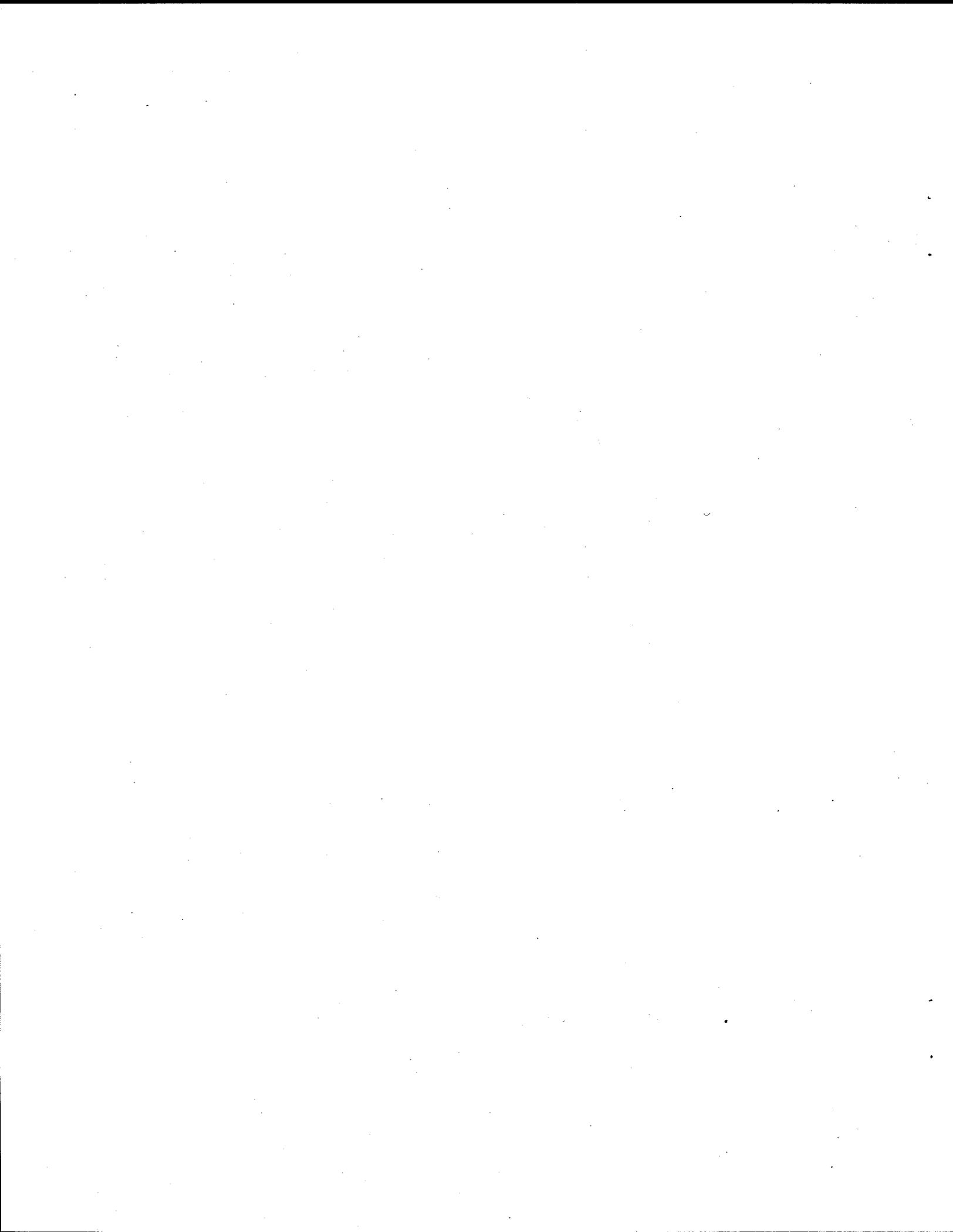
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Glossary

% 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
NPH	normal paraffin hydrocarbons
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-C-204 (Tank C-204) 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 S6067. Samples were collected by WHC on July 2, 1996 using the In Situ Vapor Sampling System (ISVS).

Sampling devices and controls provided for this job included 6 sorbent trains for selected inorganic analytes (4 sample trains and 2 field blanks), 5 SUMMA™ canisters for permanent gases and volatile organic analytes (3 samples and 2 ambient canisters), and 8 triple sorbent traps (TSTs) for semi-volatile organic analytes (4 samples, 2 field blanks, and 2 trip blanks). The samples and controls were provided to WHC on July 1, 1996. Exposed samples and controls were returned to PNNL on July 10, 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 C-204 on July 2, 1996 (Sample Job S6067) 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 ≤ 0.84 ppmv (NH_3), < 0.16 ppmv (NO_2), 0.8 ± 0.1 ppmv (NO), and 7.9 ± 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 (RSD), was $< 13\%$ 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 20 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, 100249, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent gas analysis for Tank C-204 can be found in Appendix B. In summary, only carbon dioxide at 443 ppmv was detected in the tank headspace samples. The remainder of the permanent gases were below the EQL used to calibrate the system.

2.3 Total Non-Methane Organic Compounds

The complete results of the TO-12 analysis for Tank C-204 can be found in Appendix C. In summary, the average concentration in the three tank headspace samples was 80.24 mg/m³. The average value of 80.24 mg/m³ compares to 128.64 mg/m³ for the sum of all target compounds and tentatively identified compounds (TICs) identified in the analysis of the SUMMA™ canisters.

2.4 Organic Analytes by SUMMA™ Method

The complete results of the SUMMA™ analysis for Tank C-204 can be found in Appendix D. In summary, 45 target analytes above the IDL and 130 TICs were detected in the tank headspace samples. Forty-two target analytes and 47 TICs were identified in two or more tank headspace samples. Eighty-eight TICs were not identified and were labeled as unknowns. Dodecane at 11.78 mg/m³ and tridecane at 9.51 mg/m³ accounted for 58% of the target compounds and 17% of the total compounds identified in the analysis. The total concentration of the target analytes was 36.44 mg/m³. An unknown C13 alkane at 16.22 mg/m³ and an unknown C14 alkane at 16.04 mg/m³ were the two highest concentration TICs found in two or more of the tank headspace samples. Many of the TICs can be classed as normal paraffin hydrocarbon compounds (NPH). The total concentration of TICs identified was 92.20 mg/m³ or 72% of the total concentration measured. The total concentration of all the compounds identified was 128.64 mg/m³. This compares to a total concentration of 80.24 mg/m³ measured in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 153 was analyzed in replicate for target analytes and TICs to determine analytical precision. Three of 40 target compounds and none of the 32 TICs had RPDs of less than 10%.

Thirty-nine target compounds and one TIC were observed in one or both of the ambient air samples. Many of the compounds were identified at trace levels. Several notable exceptions include methanol at 163 ppbv, acetone at 122 ppbv, and ethanol at 73 ppbv. 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.

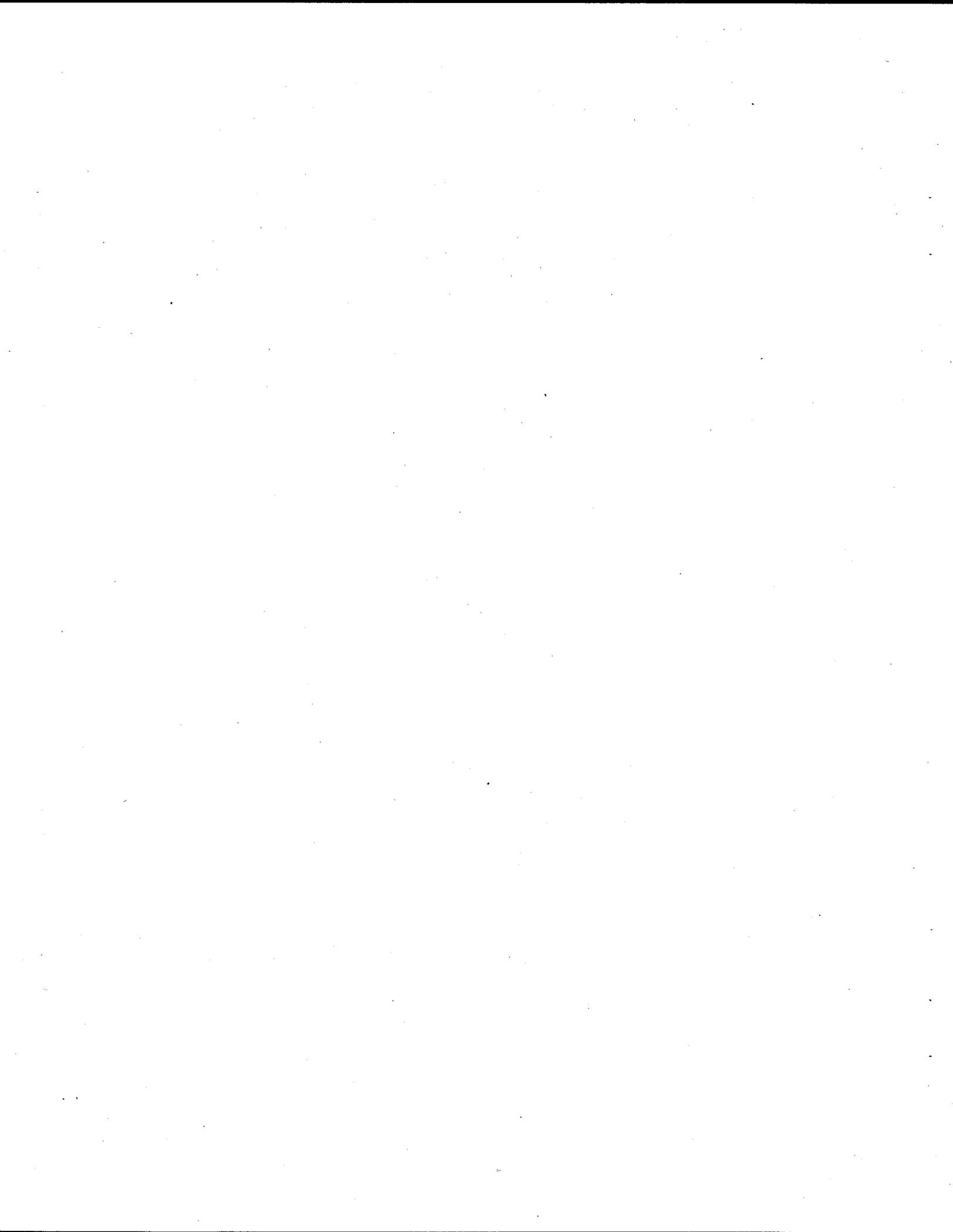
2.5 Organic Analytes by Triple Sorbent Trap Method

The complete results of the sorbent trap analysis for Tank C-204 can be found in Appendix E. In summary, 34 target analytes above the IDL and 52 TICs were detected in the tank headspace samples. Thirty-three of the target analytes and 48 TICs were observed in two or more sorbent traps. Forty-one TICs were identified and were labelled as unknowns. All of these unknowns were associated with NPH compounds. Dodecane at 2.60 mg/m³ and tridecane at 2.32 mg/m³ accounted for 50% of the target analytes and 13% of the total concentration identified by the analysis. The total concentration of the target analytes was 9.88 mg/m³ or 27% of the total concentration identified by the analyses. The predominant TICs observed in these samples were an unknown C14 alkane at 4.14 mg/m³ and an unknown C13 alkane at 3.78 mg/m³. The total concentration of the TICs was 27.00 mg/m³ or 73% of the total concentration identified by analysis. The total concentration of all the compounds identified was 36.84 mg/m³.

Triple sorbent trap sample PNL 1078 was analyzed in replicate for target analytes and TICs to determine analytical precision. Eighteen of 32 target compounds and 32 of 45 TICs had RPDs of less than 10%.

3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank C-204 on July 2, 1996 (Sample Job S6067). 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.

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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)

<u>Analyte</u>	<u>Formula</u>	<u>Procedure</u>	<u>EQL^(b)</u> <u>(μg)</u>	<u>EQL^(b)</u> <u>(ppmv)</u>	<u>Notification</u> <u>Level^(c)</u> <u>(ppmv)</u>
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 tank headspace of Tank C-204 on July 2, 1996 using the ISVS. The sample job designation number was S6067. 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 100249 (Appendix F). The inorganic samples and sample volume information were received from WHC on July 10, 1996. Analyses were completed on July 16, 1996 (gravimetric, 14 days elapsed), July 22, 1996 (ammonia, 20 days elapsed), and July 19, 1996 (nitrite, 17 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 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 ≤ 0.84 ppmv, based on all four samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from <0.06 to $0.07 \mu\text{mol}$ in front sections; blank-corrected NH_3 was not found ($\leq 0.01 \mu\text{mol}$) in back sorbent sections. Blank corrections, $0.09 \mu\text{mol}$ in front and $0.07 \mu\text{mol}$ in back sections, were about 67% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of $\pm 0.8\%$. One sample leachate was spiked after initial analysis with roughly the quantity of ammonia in the sample and yielded a percentage recovery of 84%. The initial and continuing calibration verification (CCV) standards, using NIST-traceable material, yielded percentage recoveries of 91% (ICV) and 95, 94 and 101% (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 concentration of NO_2 was < 0.16 ppmv based on all four samples. Blank-corrected NO_2^- quantities in the NO_2 sorbent traps were all $< 0.013 \mu\text{mol}$. The concentration of NO was 0.8 ± 0.1 ppmv based on all four samples. Blank Corrected NO_2^- quantities in the NO sorbent tubes averaged $0.032 \mu\text{mol}$. Nitrite blank levels used to correct data were $0.0061 \mu\text{mol}$ in front (four of four blanks analyzed) and $0.0033 \mu\text{mol}$ in back (two of four blanks analyzed) sorbent sections. The analyses of two samples were duplicated and yielded repeatabilities of $\pm 1.9\%$ and $\pm 0.6\%$. Two sample leachates were spiked with NO_2^- and yielded recoveries of 101 and 92%. 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 (Claus et al. 1994; Ligothe 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 $7.9 \pm 0.3 \text{ mg/L}$, based on dry air sample volumes (0°C and 760 torr). The result was determined from an average mass gain of 20.1 mg from all four sample trains. The blank correction applied to the results was $- 5.45 \text{ mg}$ per train, based on a mass gain of $5.45 \pm 0.21 \text{ mg}$ per two 5-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of $\pm 0.1 \text{ mg}$. Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg water was $103 \pm 2\%$ during a previous sample job (Claus et al. 1994).

Corrected for a measured tank headspace temperature of 17.8°C and pressure of 736.9 torr, the actual water vapor mass concentration from the gravimetric results was $7.1 \pm 0.2 \text{ mg/L}$. Also based on analytical results, the partial pressure of water vapor was 7.1 ± 0.2 torr, the relative humidity was $46 \pm 2\%$, and the dew point was $6.2 \pm 0.2^\circ\text{C}$.

Table A.2 List of PNNL Inorganic Samples, Controls, and Gravimetric Results
Obtained from the Headspace of Tank C-204 on 7/2/96

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>						
S6067-A07-22R	NH3/NOx/H2O	1	200.0	10.0	1.86	0.0195
S6067-A08-23R	NH3/NOx/H2O	2	200.0	10.0	1.86	0.0199
S6067-A09-24R	NH3/NOx/H2O	3	200.0	10.0	1.86	0.0206
S6067-A10-25R	NH3/H2O/H2O	4	200.0	10.0	1.86	0.0205
<u>Controls:</u>						
S6067-A15-26R	NH3/NOx/H2O Field Blank	n/a ^(b)	n/a	n/a	n/a	0.0053
S6067-A16-27R	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	0.0056

(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 C-204 on 7/2/96

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor ^(a) Concentration (ppmv)
	Front Section	Back Section	Total ^(b) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>n/a</u>	<u>1.86</u>	<u><0.84</u>
S6067-A07-22R	0.15	0.055	0.06	1.86	0.72
S6067-A08-23R	0.13	NA ^(c)	<0.06	1.86	<0.71
S6067-A09-24R	0.16	NA	0.07	1.86	0.84
S6067-A10-25R	0.10	0.067	<0.06	1.86	<0.71
<u>NO₂ Samples:</u>			<u><0.013</u>	<u>1.86</u>	<u><0.16</u>
S6067-A07-22R	0.0060	NA	<0.013	1.86	<0.16
S6067-A08-23R	0.0063	0.0031	<0.013	1.86	<0.16
S6067-A09-24R	0.0052	NA	<0.013	1.86	<0.16
S6067-A10-25R	0.0052	0.0036	<0.013	1.86	<0.16
<u>NO Samples:</u>			<u>0.032</u>	<u>1.86</u>	<u>0.8 ± 0.1</u>
S6067-A07-22R	0.0346	0.0049	0.029	1.86	0.7
S6067-A08-23R	0.0417	NA	0.036	1.86	0.9
S6067-A09-24R	0.0377	0.0063	0.032	1.86	0.8
S6067-A10-25R	0.0377	NA	0.032	1.86	0.8
<u>Gravimetric Samples:</u>			<u>14.7 mg</u>	<u>1.86</u>	<u>7.9 ± 0.3 mg/L</u>
S6067-A07-22R	n/a ^(c)	n/a	14.1	1.86	7.6
S6067-A08-23R	n/a	n/a	14.5	1.86	7.8
S6067-A09-24R	n/a	n/a	15.2	1.86	8.1
S6067-A10-25R	n/a	n/a	15.1	1.86	8.1

- (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 C-204 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 C-204, ambient air collected ~10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on July 15 and 16, 1996. Carbon dioxide at an average concentration of 443 ppmv was the only permanent gas observed above the EQL in the tank headspace samples. A replicate analysis was performed on SUMMA™ PNL 153; 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 C-204 and for Ambient Air and Ambient Air Through the ISVS Collected Near Tank C-204 in SUMMA (TM) Canisters on 7/2/96

Permanent Gas Analyte	Ambient Air Upwind		Ambient Air Through Bundle		Tank Samples					Average Concentration Tank Samples (ppmv)		
	S6067-A01.126 ^(a) PNL 126 ^(b) Concentration (ppmv)	<17 <25 429 <17 <17	S6067-A02.166 ^(a) PNL 166 ^(b) Concentration (ppmv)	<17 <25 393 <17 <17	S6067-A04.136 ^(a) PNL 136 ^(b) Concentration (ppmv)	<17 <25 427 <17 <17	S6067-A05.153 ^(a) PNL 153 ^(b) Concentration (ppmv)	<17 <25 438 <17 <17	S6067-A06.184 ^(a) PNL 184 ^(b) Concentration (ppmv)		<17 <25 463 <17 <17	S6067-A05.153 ^(a) PNL 153 ^{(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 153; 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. 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 C-204, ambient air collected ~ 10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on September 11, 1996. Concentrations in the ambient air samples ranged from <0.59 mg/m³ to 0.98 mg/m³. Concentrations in the three tank headspace samples ranged from 76.14 mg/m³ to 82.32 mg/m³ with an average concentration of 80.24 mg/m³. This compares to 128.64 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™ PNL 153; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

A deviation was made to the current procedure (PNL-TVP-08) and documented in Vapor Deviation Report #JAE082996. The following is a discussion of the deviation:

In accordance with the current method past TO-12 analyses used a calibration method based on an average response factor spanning the full dynamic range. Because the low level standards are impacted to some extent by the small amount of system blank always present, the average response factor method generates a large apparent nonlinearity introducing an unnecessary amount of level dependent error. To correct this situation, data included in this and all subsequent calibrations shall use a linear regression fit which includes both a slope and intercept. The correlation coefficient for this ten point calibration curve is 0.99996, an extremely well ordered data set. A new revision to procedure PNNL-TVP-08 currently under preparation will reflect these amendments.

Table C.1. TO-12 Results for Samples Collected Through the ISVS from the Headspace of Tank C-204 and from Ambient Air Near Tank C-204 in SUMMA (TM) Canisters on 7/2/96.

	Ambient Air Upwind	Ambient Air Through Bundle	Tank Samples			
	S6067-A01.126 ^(a)	S6067-A02.166 ^(a)	S6067-A04.136 ^(a)	S6067-A05.153 ^{(a)(d)}	S6067-A06.184 ^(a)	S6067-A05.153 ^(a)
	PNL 126 ^(b)	PNL 166 ^(b)	PNL 136 ^(b)	PNL 153 ^(b)	PNL 184 ^(b)	PNL 153 ^{(b)(c)}
	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)
	<0.59	0.98	82.32	76.14	82.26	76.35
TO-12						Average ^(d) Concentration Tank Samples (mg/m3) 80.24

Footnotes

- (a) WHC sample identification number.
- (b) PNL canister number.
- (c) Replicate analysis for PNL 153; results are not included in the calculation of average concentrations.

Appendix D

Tank Vapor Characterization: Organic Analytes by SUMMA™ Method

Appendix D

Tank Vapor Characterization: Organic Analytes by SUMMA™ Method

D.1 Sampling Methodology

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

D.2 Analytical Procedure

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

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

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

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

Table D.1 Target Organic Analytes

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

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

generation system. The operation of the permeation-tube system follows the method detailed in PNNL Technical Procedure PNL-TVP-06^(a). The standard calibration mix was analyzed using four aliquot sizes ranging from 30 mL to 200 mL, and a response factor for each compound was calculated. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. Instrument detection limits and EQLs have been determined. Methanol, ethanol, and 1,3-butadiene are not currently included in the method performance section of the procedure for System 1; however, these 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.

D.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "high-sensitivity tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated using a standard gas mixture containing 67 organic compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d₃, 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/m^3 :

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

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/m^3 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 July 10, 1996 under WHC COC form 100247 (see Appendix F). Samples were analyzed on August 27, August 30, and September 12, 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 C-204 and through the ISVS near Tank C-204 are presented in Table D.4.

Table D.2 lists the quantitative results for compounds listed as target analytes and TICs. Target compounds not listed in Table D.2 were not detected in any of the tank headspace samples above the compound IDL. Due to the high concentration of organic compounds in the tank headspace samples, all tank samples were reanalyzed at a 1:5 dilution ratio. Target compounds in Table D.2 marked with "*" flag were values measured in the diluted samples.

The analyses identified 45 target analytes above the IDL and 130 TICs in the tank headspace samples. Forty-two target analytes and 47 TICs were identified in two or more tank headspace samples. Eighty-eight TICs were not identified and were labeled as unknowns. Dodecane at $11.78 \text{ mg}/\text{m}^3$ and tridecane at $9.51 \text{ mg}/\text{m}^3$ accounted for 58% of the target compounds and 17% of the total compounds identified in the analysis. The total concentration of the target analytes was $36.44 \text{ mg}/\text{m}^3$. An unknown C13 alkane at $16.22 \text{ mg}/\text{m}^3$ and an unknown C14 alkane at $16.04 \text{ mg}/\text{m}^3$ were the two highest concentration TICs found in two or more of the tank headspace samples. Many of the TICs can be classed as NPH compounds. The total concentration of TICs identified was $92.20 \text{ mg}/\text{m}^3$ or

72% of the total concentration measured. The total concentration of all the compounds identified was 128.64 mg/m³. This compares to a total concentration of 80.24 mg/m³ measured in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 153 was analyzed in replicate for target analytes and TICs to determine analytical precision. Three of 40 target compounds and none of the 32 TICs had RPDs of less than 10%.

Thirty-nine target compounds and one TIC were observed in one or both of the ambient air samples. Many of the compounds were identified at trace levels. Several notable exceptions include methanol at 163 ppbv, acetone at 122 ppbv, and ethanol at 73 ppbv. Trace levels of many of the target analytes may be false positives due to the fact that some of the compounds were found in the CCB above the EQL and are greater than 20 times the concentration found in the sample. These compounds are flagged with a "B" in the tables.

The following procedural changes and observations were noted during the analysis of Tank C-204:

Methanol, ethanol, and 1,3-butadiene are not currently included in the method performance section of the procedure for System 1; however, these 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.

Batch 8/27/96:

This analytical sequence was run using 100 ml volumes to quantify target compounds in each tank sample and ambient sample.

Three target compounds (1,1,2,2-tetrachloroethane at 38.53%, tridecane at 34.0%, and tetradecane at 47.3%) surpassed the 30% RSD acceptance criteria for the initial calibration. The compound 1,1,2,2-tetrachloroethane was not found in the tank samples. Tridecane was found in the samples of ambient air (S6067-A01.126 and S6067-A02.166) at concentrations between the IDL and the EQL. Tetradecane was found in one sample of ambient air (S6067-A02.166) at a concentration between the IDL and the EQL. Tridecane and tetradecane were found in tank samples S6067-A04.136 and S6067-A05.153 at concentrations exceeding the upper quantitation limit (UQL). Four target compounds (acetonitrile, acetone, pyridine, and tetradecane) were outside the 25% difference (% D) acceptance criteria for the CCV sample. However, the CCV passed the procedural criterion requiring $\pm 25\%$ D passage for 85% of all target compounds. Acetone was found in all samples at concentrations between the EQL and the UQL. These concentrations may be over estimated. Acetonitrile was found in ambient air sample S6067-A01.126 at a concentration between the IDL and the EQL and in tank samples S6067-A04.136 and S6067-A05.153 at concentrations between the EQL and the UQL. Pyridine was found in the samples S6067-A01.126 and S6067-A04.136 at concentrations between the IDL and the EQL. Target compound methylene chloride was found in the continuing calibration blank (CCB) above the EQL, but its concentration was less than 2 ppbv. This compound was also found in initial calibration blank (ICB) above its EQL.

The internal standard quantification area percent recoveries for the last three samples and the first blank exceeded the acceptance criterion ($50\% < \text{quantification} < 200\%$) allowed by procedure PNL-TVP-03, Rev. 2. The changes in the internal standard areas was caused by water induced fatigue. This problem is routinely observed with the HP5972 GC/MS system because of its poor pumping capacity. Target compounds found in these samples could be affected. This problem will continue until a larger GC/MS system is used in the analysis.

Batch 8/30/96:

This analytical sequence was run using 100 ml volumes to quantify target compounds in each tank sample.

Three target compounds (1,1,2,2-tetrachloroethane at 38.53%, tridecane at 34.0%, and tetradecane at 47.3%) surpassed the 30% RSD acceptance criteria for the initial calibration. The compound 1,1,2,2-tetrachloroethane was not found in the tank samples. Tridecane was found in tank sample S6067-A05.153 at a concentration between the EQL and the UQL and in the tank sample S6067-A06.184 at a concentration exceeding the UQL. Tetradecane was found in the tank samples S6067-A05.153 and S6067-A06.184 at concentrations between the EQL and the UQL.

Seven target compounds (acetonitrile, butanenitrile, 1,1,2,2-tetrachloroethane, dodecane, pyridine, tridecane and tetradecane) were outside the 25% D acceptance criteria for the CCV sample. However, the CCV passed the procedural criterion requiring $\pm 25\%$ D passage for 85% of all target compounds. The compound 1,1,2,2-tetrachloroethane, as mentioned above, was not found in the tank samples. Acetonitrile, tetradecane and butanenitrile were found in both tank samples at concentrations between the EQL and the UQL. These concentrations may be over estimated. Dodecane was found in both tank samples at concentrations exceeding the UQL. Tridecane was found in tank sample S6067-A05.153 at a concentration between the EQL and the UQL, and in tank sample S6067-A06.184 at a concentration above the UQL. Pyridine was found in samples S6067-A05.153 and S6067-A06.184 at concentrations between the IDL and the EQL.

Target compound methylene chloride was found in the CCB above the EQL, but the concentration was less than 2 ppbv. This compound was also found in ICB above the EQL.

Batch 9/12/96:

This analytical sequence was run using 100 ml volumes to quantify target compounds in each tank sample. The samples were diluted previously 1:5 volume/volume.

Two target compounds (1,2-dichloro-1,1,2,2-tetrafluoroethane at 37.51% and tetradecane at 40.68%) surpassed the 30% RSD acceptance criteria for the initial calibration. The compound 1,2-dichloro-1,1,2,2-tetrafluoroethane was not found in the tank samples. Tetradecane was found in tank samples S6067-A04.136, S6067-A05.153 and S6067-A06.184 at concentrations between the EQL and the UQL.

Four target compounds (1,2-dichloro-1,1,2,2-tetrafluoroethane, butane, bromomethane, and 1,3-butadiene) were outside the 25% D acceptance criteria for the CCV sample. However,

the CCV passed the procedural criterion requiring $\pm 25\%$ D passage for 85% of all target compounds.

The compound 1,2-dichloro-1,1,2,2-tetrafluoroethane, as was mentioned above, was not found in the tank samples. Butane and 1,3-butadiene were found in all tank samples at concentrations between the EQL and the UQL, with the exception of tank sample S6067-A05.153, where 1,3-butadiene was not found at a concentration above the EQL. Bromomethane was found in tank sample S6067-A04.136 at a concentration between the IDL and the EQL.

Target compounds (methylene chloride, 1,3-dichlorobenzene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene) were found in the CCB above the EQL, but their concentrations were less than 2 ppbv. The compounds decane and 1,4-dichlorobenzene were also found in the ICB above the EQL (at concentrations less than 2 ppbv).

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 C-204 in SUMMA Canisters Collected on 7/2/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6067-A05.153 ^{(c)(d)} ISVS		S6067-A06.184 ^(c) ISVS		S6067-A04.136 ^(c) ISVS		Mean and Standard Deviation						
				(mg/m ³)	(ppbv) Flag	(mg/m ³)	(ppbv) Flag	(mg/m ³)	(ppbv) Flag	(mg/m ³) St. Dev.	(ppbv) St. Dev.					
Dichlorodifluoromethane	75-71-8	121	4.6	0.010	1.8	J	0.006	1.1	J	0.016	3.0	J	0.011	0.005	2.0	0.93
Chloromethane	74-87-3	50	5.0	0.004	1.9	J	0.003	1.4	J	0.011	4.7	J	0.006	0.004	2.6	1.8
Methanol	67-56-1	32	5.3	0.217	152	Y	0.130	91	Y	0.500	350	Y	0.282	0.193	197	135
Butane	106-97-8	58	5.9	0.320	123		0.177	68		0.501	193		0.333	0.162	128	63
Ethanol	64-17-5	46	6.9	0.284	138	Y	0.178	87	Y	0.458	223	Y	0.307	0.141	149	69
Acetonitrile	75-05-8	41	7.4	0.205	112		0.116	63		0.285	155		0.202	0.085	110	46
Acetone	67-64-1	58	7.9	0.881	340		0.249	96		1.795	692		0.975	0.777	376	300
Trichlorofluoromethane	75-69-4	137	8.3	0.028	4.6	J	0.022	3.5	J	0.038	6.3	J	0.029	0.008	4.8	1.4
Pentane	109-66-0	72	9.0	0.030	9.4	J	0.019	5.8	J	0.040	13		0.030	0.011	9.3	3.4
Methylene Chloride	75-09-2	85	9.7	0.023	6.1	B	0.021	5.5	B	0.026	6.8	B	0.023	0.003	6.1	0.67
1,1,1-Trichloro-2,2,2-trifluoroethane	76-13-1	187	10.2	0.177	21		0.136	16		0.195	23		0.169	0.030	20	3.6
Propanol	71-23-8	60	10.9	0.806	300		0.439	163		1.069	398		0.771	0.317	287	118
Propanenitrile	107-12-0	55	10.9	0.063	26		0.039	16		0.083	34		0.061	0.022	25	9.0
2-Butanone	78-93-3	72	12.5	0.462	143		0.235	73		0.519	161		0.405	0.151	126	47
Hexane	110-54-3	86	13.8	0.040	10		0.030	7.8	J	0.051	13		0.040	0.011	10	2.7
Chloroform	67-66-3	119	13.9	0.003	0.51	J	0.002	0.39	J	0.004	0.73	J	0.003	0.001	0.54	0.17
Tetrahydrofuran	109-99-9	72	14.7	0.134	42		0.052	16		0.080	25		0.088	0.042	27	13
Butanenitrile	109-74-0	69	15.8	0.160	52		0.103	33		0.222	72		0.162	0.060	52	19
1,1,1-Trichloroethane	71-55-6	133	15.9	0.003	0.54	U	0.002	0.33	J	0.004	0.63	J	0.003	e	0.48	e
1-Butanol	71-36-3	74	16.3	2.726	824	*	4.444	1343		3.281	991	*	3.484	0.877	1053	265
Benzene	71-43-2	78	16.8	0.010	3.0	J	0.007	2.0	J	0.012	3.4	J	0.010	0.002	2.8	0.71
Carbon Tetrachloride	56-23-5	154	17.1	0.003	0.50	U	0.001	0.16	J	0.003	0.50	U	e	e	e	e
Cyclohexane	110-82-7	84	17.3	0.046	12		0.034	9.2	J	0.057	15		0.046	0.012	12	3.1
Heptane	142-82-5	100	19.3	0.075	17		0.050	11		0.078	17		0.068	0.015	15	3.4
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.020	4.5	J	0.011	2.4	J	0.023	5.2	J	0.018	0.006	4.0	1.5
Pyridine	110-86-1	79	20.7	0.019	5.3	U	0.006	1.6	J	0.005	1.5	J	0.006	e	1.6	e
Pentanenitrile	110-59-8	83	21.6	0.006	1.6	J	0.005	1.2	J	0.007	1.8	J	0.006	0.001	1.5	0.32
Toluene	108-88-3	92	22.6	0.020	4.8	J	0.015	3.6	J	0.015	3.7	J	0.016	0.003	4.0	0.66
Octane	111-65-9	114	24.7	0.047	9.2		0.036	7.1		0.038	7.5		0.041	0.006	7.9	1.1
Hexanenitrile	628-73-9	97	27.1	0.009	2.1	J	0.002	0.51	J	0.007	1.5	J	0.006	0.003	1.4	0.78
Ethylbenzene	100-41-4	106	27.7	0.005	1.0	J	0.004	0.76	J	0.004	0.92	J	0.004	0.001	0.89	0.12
p/m-Xylene	106-42-3	106	28.1	0.015	3.1	J	0.013	2.7	J	0.012	2.6	J	0.013	0.001	2.8	0.27

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 C-204 in SUMMA Canisters Collected on 7/2/96

Target Analytes ^(a)	CAS	MW	Ret Time (mg/m ³)	S6067-A05.153 ^{(c)(d)} ISVS		S6067-A06.184 ^(c) ISVS		S6067-A04.136 ^(c) ISVS		Mean and Standard Deviation				
				(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	St. Dev.	(ppbv)
Cyclohexanone	108-94-1	98	28.6	0.076	17	0.040	9.2	J	0.072	16	0.063	0.020	14	4.5
Styrene	100-42-5	104	29.1	0.004	0.77	0.004	0.79	J	0.003	0.57	0.003	0.001	0.71	0.12
o-Xylen	95-47-6	106	29.4	0.005	0.97	0.006	1.2	J	0.004	0.87	0.005	0.001	1.0	0.17
Norane	111-84-2	128	29.8	0.054	9.5	0.047	8.2		0.052	9.0	0.051	0.004	8.9	0.64
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.0	0.002	0.34	0.002	0.34	J	0.002	0.34	e	e	e	e
1,3,5-Trimethylbenzene	108-67-8	120	33.0	0.002	0.34	0.002	0.31	J	0.002	0.34	e	e	e	e
1,2,4-Trimethylbenzene	95-63-6	120	34.2	0.007	1.3	0.007	1.2	J	0.008	1.5	0.007	0.001	1.3	0.14
Decane	124-18-5	142	34.5	0.856	135	0.628	99		0.965	152	0.816	0.172	129	27
Undecane	1120-21-4	156	38.8	2.944	422	3.479	499	*	2.626	376	3.016	0.431	432	62
Dodecane	112-40-3	170	42.8	10.931	1437	12.899	1696	*	11.497	1544	11.775	1.013	1559	130
Tridecane	629-50-5	184	46.5	7.357	894	9.682	1176	*	11.497	1397	9.512	2.075	1132	289
Tetradecane	629-59-4	198	50.0	2.548	288	2.037	230	*	4.508	509	3.031	1.305	342	147
1,3-Butadiene	106-99-0	54	5.8	0.499	207	0.285	118	Y	0.831	345	0.538	0.275	223	114
Tentatively Identified Compounds^(b)														
Propene	115-07-1	42	4.4	0.403	215	0.183	98	N	0.371	198	0.319	0.119	170	63
Acetaldehyde	75-07-0	44	5.2	0.211	107	0.147	75	N	nd	nd	0.179	e	91	e
2-Butene, (E)-	624-64-6	56	6.1	nd	nd	nd	nd		0.111	44	e	e	e	e
1-Propene, 2-methyl-	115-11-7	56	6.4	0.163	65	nd	nd		0.253	101	0.208	e	83	e
Propanal	123-38-6	58	8.0	0.436	169	0.344	133	N	0.627	242	0.469	0.144	181	56
3-Buten-2-one	78-94-4	70	11.9	0.143	46	0.161	52	N	0.320	102	0.208	0.097	67	31
Butanal	123-72-8	72	12.3	3.823	1189	2.577	802	N	5.357	1667	3.919	1.393	1219	433
1,3-Propanediol, dinitrate	3457-90-7	166	13.9	0.134	18	nd	nd		nd	nd	e	e	e	e
1,2,3-Propanetriol, 1-nitrate	624-43-1	137	14.0	nd	nd	nd	nd		0.162	26	e	e	e	e
Unknown			14.6	0.956	f	nd	nd		nd	nd	e	e	e	e
Nitric acid, propyl ester	627-13-4	105	19.2	0.762	162	0.401	86	N	0.917	196	0.693	0.265	148	57
Nitric acid, butyl ester	928-45-0	119	24.7	0.263	49	0.185	35	N	0.260	49	0.236	0.044	44	8.4
Butane, 1-nitro-	627-05-4	103	25.1	2.065	449	1.163	253	N	2.224	484	1.817	0.572	395	124
Unknown Alkane			31.5	nd	nd	nd	nd		0.172	f	e	e	e	e
Cyclohexane, 1,1,2,3-tetramethyl-	6783-92-2	140	33.3	nd	nd	0.399	64	N	nd	nd	e	e	e	e
Unknown C10 Alkene/Cycloalkane			33.3	0.418	f	nd	nd		0.330	f	0.374	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 C-204 in SUMMA Canisters Collected on 7/2/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time (mg/m ³)	S6067-A05.153 ^{(c)(d)} ISVS		S6067-A06.184 ^(c) ISVS		S6067-A04.136 ^(c) ISVS		Mean and Standard Deviation (mg/m ³)	St. Dev. (ppbv)	St. Dev.
				(ppbv)	Flag	(ppbv)	Flag	(mg/m ³)	(ppbv)			
Unknown C10 Alkene/Cycloalkane			34.0	0.176	f	nd	nd	0.178	f	0.177	e	e
Cyclohexane, 1,4-dimethyl-	589-90-2	112	34.2	0.279	56	N	nd	nd	nd	e	e	e
Cyclohexane, 1-methyl-3-propyl-	4291-80-9	140	34.2	nd	nd	0.192	31	N	nd	e	e	e
Unknown C10 Alkene/Cycloalkane			34.2	nd	nd	nd	nd	0.283	f	e	e	e
Unknown C10 Alkene/Cycloalkane			35.4	0.182	f	nd	nd	nd	nd	e	e	e
Unknown Alkane			35.4	nd	nd	nd	nd	0.213	f	e	e	e
Decane, 4-methyl-	2847-72-5	156	35.6	nd	nd	1.372	197	N	nd	e	e	e
Unknown C11 Alkane			35.6	1.763	f	nd	nd	1.936	f	1.850	e	e
Unknown Alkane			36.1	0.232	f	0.197	f	nd	nd	0.214	e	e
Unknown C11 Alkene/Cycloalkane			36.3	0.574	f	nd	nd	nd	nd	e	e	e
Unknown C10 Alkene/Cycloalkane			36.4	nd	nd	1.072	f	nd	nd	e	e	e
Unknown C10 Alkene/Cycloalkane			36.4	nd	nd	nd	nd	1.462	f	e	e	e
Unknown C10 Alkene/Cycloalkane			36.7	nd	nd	0.282	f	nd	nd	e	e	e
Unknown C11 Alkene/Cycloalkane			36.7	0.344	f	nd	nd	nd	nd	e	e	e
Unknown Alkene/Cycloalkane			36.7	nd	nd	nd	nd	0.365	f	e	e	e
Unknown C11 Alkane			37.0	0.641	f	0.511	f	nd	nd	0.576	e	e
Unknown C11 Alkane			37.0	nd	nd	nd	nd	0.671	f	e	e	e
Unknown C11 Alkane			37.2	nd	nd	0.422	f	nd	nd	e	e	e
Decane, 4-methyl-	2847-72-5	156	37.2	0.693	100	N	nd	nd	nd	e	e	e
Unknown Alkane			37.2	nd	nd	nd	nd	0.696	f	e	e	e
Decane, 2-methyl-	6975-98-0	156	37.3	nd	nd	0.594	85	N	nd	e	e	e
Unknown C11 Alkane			37.3	0.901	f	nd	nd	nd	nd	e	e	e
Decane, 2-methyl-	6975-98-0	156	37.3	nd	nd	nd	nd	0.993	143	e	e	e
Unknown C11 Alkene/Cycloalkane			37.4	0.500	f	0.425	f	0.548	f	0.491	0.062	e
Unknown C11 Alkane			37.6	0.785	f	0.610	f	0.846	f	0.747	0.122	e
Naphthalene, decahydro-, trans-	493-02-7	138	37.9	1.228	199	N	1.101	179	N	1.218	0.112	198
Unknown C11 Alkene/Cycloalkane			38.1	nd	nd	0.475	f	nd	nd	e	e	e
Bicyclo[4.1.0]heptan-3-one, 4,7-trimethyl	4176-04-9	152	38.2	0.583	86	N	nd	nd	nd	e	e	e
Unknown			38.2	nd	nd	nd	nd	0.608	f	e	e	e
Unknown Alkene/Cycloalkane			38.6	1.471	f	nd	nd	1.475	f	1.473	e	e
5-Undecene	4941-53-1	154	38.6	nd	nd	1.040	151	N	nd	e	e	e
Unknown C11 Alkene/Cycloalkane			38.7	nd	nd	0.519	f	nd	nd	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 C-204 in SUMMA Canisters Collected on 7/2/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time (mg/m ³)	S6067-A05.153 ^{(c)(d)} ISVS		S6067-A06.184 ^(c) ISVS		S6067-A04.136 ^(c) ISVS		Mean and Standard Deviation	
				(ppbv)	Flag	(mg/m ³)	Flag	(ppbv)	Flag	(mg/m ³)	St. Dev.
Unknown C12 Alkene/Cycloalkane			38.7	0.617	f	nd	nd	nd	nd	e	e
Unknown C11 Alkene/Cycloalkane			39.3	2.307	f	1.735	f	2.143	f	2.062	0.295
Unknown C12 Alkane			39.6	2.440	f	1.731	f	2.217	f	2.129	0.363
Unknown Cycloalkene			39.9	1.355	f	0.993	f	0.642	f	0.997	0.356
Unknown C12 Alkane			40.0	2.158	f	1.398	f	1.698	f	1.751	0.383
Naphthalene, decalhydro-2-methyl-	2958-76-1	152	40.3	2.833	418	N	2.006	296	N	e	e
Pulegone	89-82-7	152	40.4	nd	nd	nd	nd	2.511	370	e	e
Cyclohexane, pentyl-	4292-92-6	154	40.8	2.856	415	N	1.826	266	N	2.414	0.530
Naphthalene, decalhydro-2-methyl-	2958-76-1	152	41.1	5.511	812	N	3.494	515	N	4.646	1.038
Undecane, 4-methyl-	2980-69-0	170	41.2	nd	nd	nd	0.838	110	N	e	e
Unknown C12 Alkane			41.3	1.482	f	nd	nd	nd	nd	e	e
Unknown C13 Alkene/Cycloalkane			41.3	nd	nd	nd	nd	1.232	f	e	e
Undecane, 2-methyl-	7045-71-8	170	41.4	nd	nd	nd	2.534	334	N	e	e
Unknown C12 Alkane			41.4	4.372	f	nd	nd	3.880	f	4.126	e
Undecane, 3-methyl-	1002-43-3	170	41.7	2.072	273	N	1.155	152	N	1.691	0.478
Unknown C12 Alkene/Cycloalkane			41.8	nd	nd	nd	0.257	f	f	0.342	e
Unknown Alkene/Cycloalkane			41.9	nd	nd	nd	0.390	f	f	0.514	e
Unknown C12 Alkene/Cycloalkane			42.1	0.688	f	0.423	f	0.353	f	0.488	0.177
Unknown C12 Alkene/Cycloalkane			42.5	1.948	f	nd	nd	nd	nd	e	e
Unknown Alkyl Decahydronaphthalene			42.5	nd	nd	nd	1.077	f	f	e	e
Unknown Alkene/Cycloalkane			42.5	nd	nd	nd	nd	nd	f	e	e
Unknown C12 Alkene/Cycloalkane			43.0	0.477	f	0.773	f	nd	nd	0.625	e
Unknown Alkene/Cycloalkane			43.0	nd	nd	nd	nd	1.310	f	e	e
Unknown Alkyl Decahydronaphthalene			43.2	nd	nd	nd	1.692	f	f	e	e
Naphthalene, decalhydro-2,3-dimethyl-	1008-80-6	166	43.2	3.071	414	N	nd	nd	nd	e	e
Naphthalene, decalhydro-2,6-dimethyl-	1618-22-0	166	43.2	nd	nd	nd	nd	nd	nd	e	e
Unknown C13 Alkane			43.4	19.890	f	12.557	f	nd	nd	16.223	e
Unknown Alkane			43.4	nd	nd	nd	nd	23.956	f	e	e
Unknown C12 Alkene/Cycloalkane			43.7	nd	nd	nd	1.357	f	f	e	e
Naphthalene, decalhydro-2,6-dimethyl-	1618-22-0	166	44.0	1.538	208	N	nd	nd	nd	e	e
Unknown Cycloalkene			44.0	nd	nd	nd	1.514	f	f	e	e
Unknown			44.0	3.111	f	nd	nd	2.638	f	2.875	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 C-204 in SUMMA Canisters Collected on 7/2/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time (mg/m ³)	S6067-A05.153 ^{(a)(b)} ISVS		S6067-A06.184 ^(a) ISVS		S6067-A04.136 ^(a) ISVS		Mean and Standard Deviation	
				(ppbv)	Flag	(mg/m ³)	Flag	(mg/m ³)	Flag	(mg/m ³)	St. Dev. (ppbv)
Unknown Alkyl Decahydronaphthalene			44.4	nd	nd	1.850	f	nd	nd	e	e
Unknown Cycloalkane			44.4	nd	nd	nd	nd	3.180	f	e	e
Unknown C13 Alkene/Cycloalkane			44.8	nd	nd	6.137	f	nd	nd	e	e
1-Octadecanol	112-92-5	270	44.8	11.575	960	nd	nd	nd	nd	e	e
1-Hexadecanol	36653-82-4	242	44.8	nd	nd	nd	nd	11.402	1055	e	e
Unknown Alkyl Decahydronaphthalene			45.0	nd	nd	0.457	f	nd	nd	e	e
Unknown			45.0	0.739	f	nd	nd	0.841	f	0.790	e
Unknown C13 Alkene/Cycloalkane			45.2	3.237	f	1.679	f	nd	nd	2.458	e
Unknown Alkane			45.3	nd	nd	nd	nd	3.042	f	e	e
Unknown C14 Alkane			45.5	nd	nd	1.135	f	nd	nd	e	e
Unknown Alkane			45.5	2.441	f	nd	nd	2.368	f	2.404	e
Unknown C14 Alkane			45.7	20.796	f	11.290	f	nd	nd	16.043	e
Unknown Alkane			45.7	nd	nd	nd	nd	21.930	f	e	e
Unknown Alkene/Cycloalkane			46.1	1.698	f	0.971	f	1.545	f	1.405	0.383
Unknown C13 Alkene/Cycloalkane			46.7	1.492	f	0.823	f	1.566	f	1.294	0.409
Cyclohexane, 1,1,2-trimethyl-	7094-26-0	126	46.9	nd	nd	1.500	267	nd	nd	e	e
Unknown C14 Alkene/Cycloalkane			46.9	2.754	f	nd	nd	2.921	f	2.838	e
Unknown Alkene/Cycloalkane			47.2	nd	nd	nd	nd	0.670	f	e	e
Unknown C14 Alkane			47.3	2.669	f	1.476	f	nd	nd	2.073	e
Tridecane, 6-methyl-	13287-21-3	198	47.3	nd	nd	nd	nd	2.793	316	e	e
Unknown			47.7	nd	nd	0.183	f	nd	nd	e	e
(7E,9E)-Dodecadienal	180	180	47.7	0.538	67	nd	nd	nd	nd	e	e
Unknown Alkene/Cycloalkane			47.7	nd	nd	nd	nd	0.332	f	e	e
Unknown Alkane			47.9	nd	nd	nd	nd	0.299	f	e	e
Unknown C14 Alkene/Cycloalkane			48.3	1.310	f	0.692	f	nd	nd	1.001	e
Unknown Ketone			48.4	nd	nd	nd	nd	1.284	f	e	e
Unknown C14 Alkene/Cycloalkane			48.5	1.176	f	0.658	f	nd	nd	0.917	e
Unknown Cycloalkane			48.6	nd	nd	nd	nd	1.255	f	e	e
Unknown C13 Alkene/Cycloalkane			48.6	2.266	f	1.219	f	2.288	f	1.924	0.611
Unknown C14 Alkene/Cycloalkane			48.8	nd	nd	0.624	f	nd	nd	e	e
Unknown Alkane			48.8	1.152	f	nd	nd	1.069	f	1.110	e
Unknown C14 Alkane			49.1	0.553	f	nd	nd	nd	nd	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 C-204 in SUMMA Canisters Collected on 7/2/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time (min)	S6067-A05.153 ^{(c)(d)} ISVS		S6067-A06.184 ^(c) ISVS		S6067-A04.136 ^(c) ISVS		Mean and Standard Deviation		
				(mg/m ³)	(ppbv) Flag	(mg/m ³)	(ppbv) Flag	(mg/m ³)	(ppbv) Flag	(mg/m ³)	St. Dev. (ppbv)	St. Dev.
Tridecane, 3-methyl-	6418-41-3	198	49.1	nd	nd	0.259	29	N	nd	nd	e	e
Unknown Alkane			49.1	nd	nd	nd	nd	nd	0.542	f	e	e
Unknown Cycloalkane			49.2	nd	nd	nd	nd	nd	0.258	f	e	e
Dodecane, 2,6,10-trimethyl-	3891-98-3	212	49.4	nd	nd	3.909	413	N	nd	nd	e	e
Unknown C15 Alkane			49.4	7.050	f	nd	nd	nd	nd	nd	e	e
Unknown Alkane			49.4	nd	nd	nd	nd	nd	7.555	f	e	e
Bicyclo[4.1.0]heptane, 2-methyl-7-pentyl	55937-92-3	180	49.6	1.276	159	N	nd	nd	nd	nd	e	e
Unknown Alkene/Cycloalkane			49.6	nd	nd	0.724	f	nd	1.319	f	1.021	e
Unknown Alkene/Cycloalkane			49.8	nd	nd	nd	nd	nd	0.486	f	e	e
Unknown C14 Alkane			50.3	nd	nd	0.406	f	nd	nd	nd	e	e
Unknown Alkane			50.3	nd	nd	nd	nd	nd	0.801	f	e	e
Unknown Alkene/Cycloalkane			50.5	nd	nd	nd	nd	nd	0.380	f	e	e
Cyclohexane, 1,1,3-trimethyl-2-(3-methyl	54965-05-8	210	50.7	0.821	88	N	53	N	nd	nd	0.660	e
Unknown Alkene/Cycloalkane			50.7	nd	nd	nd	nd	nd	0.852	f	e	e
Unknown C15 Alkane			52.2	nd	nd	0.829	f	nd	nd	nd	e	e
Unknown C16 Alkane			52.2	1.391	f	nd	nd	nd	nd	nd	e	e
Unknown Alkane			52.2	nd	nd	nd	nd	nd	1.615	f	e	e
Pentadecane	629-62-9	212	53.3	0.204	22	N	nd	nd	0.224	24	N	23

Data Quality Flags

- B Compound found in associated laboratory blank.
- J Target compound detected above the IDL but below the EQL.
- N Denotes tentatively identified compound
- U Target compound not detected at or above the IDL.
- Y Initial calibration and CCV was performed; however, the analyte was not part of the current operating procedure.
- * Flag denotes diluted value used in table

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 on a Single SUMMATM Canister Collected from the Headspace of Tank C-204 on 7/2/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6067-A05.153 ^(c) ISVS						Relative Percent
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	Difference ^(d) %
Dichlorodifluoromethane	75-71-8	121	4.6	0.010	1.8	J	0.004	0.78	J	81
Chloromethane	74-87-3	50	5.0	0.004	1.9	J	0.002	1.0	J	58
Methanol	67-56-1	32	5.3	0.217	152	Y	0.143	100	Y	41
Butane	106-97-8	58	5.9	0.320	123		0.152	58		71
Ethanol	64-17-5	46	6.9	0.284	138	Y	0.163	79	Y	54
Acetonitrile	75-05-8	41	7.4	0.205	112		0.103	56		66
Acetone	67-64-1	58	7.9	0.881	340		0.268	103		107
Trichlorofluoromethane	75-69-4	137	8.3	0.028	4.6	J	0.016	2.5	J	58
Pentane	109-66-0	72	9.0	0.030	9.4	J	0.014	4.3	J	74
Methylene Chloride	75-09-2	85	9.7	0.023	6.1	B	0.019	4.9	B,J	21
1,1,1-Trichloroethane	76-13-1	187	10.2	0.177	21		0.087	10		69
Propanol	71-23-8	60	10.9	0.806	300		0.389	145		70
Propanenitrile	107-12-0	55	10.9	0.063	26		0.035	14	J	58
2-Butanone	78-93-3	72	12.5	0.462	143		0.235	73		65
Hexane	110-54-3	86	13.8	0.040	10		0.022	5.7	J	59
Chloroform	67-66-3	119	13.9	0.003	0.51	J	0.001	0.23	J	77
Tetrahydrofuran	109-99-9	72	14.7	0.134	42		0.052	16		88
Butanenitrile	109-74-0	69	15.8	0.160	52		0.102	33		44
1,1,1-Trichloroethane	71-55-6	133	15.9	0.003	0.54	U	0.001	0.14	J	
1-Butanol	71-36-3	74	16.3	2.726	824	*	2.773	838		2
Benzene	71-43-2	78	16.8	0.010	3.0	J	0.004	1.2	J	82
Cyclohexane	110-82-7	84	17.3	0.046	12		0.025	6.7	J	59
Heptane	142-82-5	100	19.3	0.075	17		0.032	7.1		81
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.020	4.5	J	0.009	2.1	J	74
Pyridine	110-86-1	79	20.7	0.019	5.3	U	0.012	3.3	J	
Pentanenitrile	110-59-8	83	21.6	0.006	1.6	J	0.004	1.1	J	30
Toluene	108-88-3	92	22.6	0.020	4.8	J	0.006	1.5	J	102
Octane	111-65-9	114	24.7	0.047	9.2		0.016	3.2	J	98
Hexanenitrile	628-73-9	97	27.1	0.009	2.1	J	0.006	1.3	J	44
Ethylbenzene	100-41-4	106	27.7	0.005	1.0	J	0.002	0.47	J	72
p/m-Xylene	106-42-3	106	28.1	0.015	3.1	J	0.007	1.5	J	68
Cyclohexanone	108-94-1	98	28.6	0.076	17		0.022	5.0	J	111
Styrene	100-42-5	104	29.1	0.004	0.77	J	0.005	1.1	J	36
o-Xylene	95-47-6	106	29.4	0.005	0.97	J	0.004	0.92	J	7
Nonane	111-84-2	128	29.8	0.054	9.5		0.027	4.8		66
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.0	0.002	0.34	U	0.002	0.31	J	
1,3,5-Trimethylbenzene	108-67-8	120	33.0	0.002	0.34	U	0.003	0.46	J	
1,2,4-Trimethylbenzene	95-63-6	120	34.2	0.007	1.3	J	0.005	1.0	J	26
Decane	124-18-5	142	34.5	0.856	135		0.376	59		78
1,3-Dichlorobenzene	541-73-1	147	34.8	0.002	0.27	U	0.002	0.37	J	
1,4-Dichlorobenzene	106-46-7	147	35.0	0.002	0.27	U	0.004	0.58	J	
1,2-Dichlorobenzene	95-50-1	147	36.1	0.002	0.27	U	0.004	0.58	J	
Undecane	1120-21-4	156	38.8	2.944	422	*	2.691	386		9
1,2,4-Trichlorobenzene	120-82-1	181	42.3	0.003	0.35	U	0.013	1.6	J	
Dodecane	112-40-3	170	42.8	10.931	1437	*	6.183	813	E	55
Hexachloro-1,3-butadiene	87-68-3	261	44.1	0.005	0.40	U	0.006	0.49	J	
Tridecane	629-50-5	184	46.5	7.357	894	*	4.079	496		57
Tetradecane	629-59-4	198	50.0	2.548	288	*	1.070	121		82
1,3-Butadiene	106-99-0	54	5.8	0.499	207	Y	0.246	102	Y	68

Table D.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis on a Single SUMMATM Canister Collected from the Headspace of Tank C-204 on 7/2/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6067-A05.153 ^(c) ISVS						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Propene	115-07-1	42	4.4	0.403	215	N	nd	nd		
Acetaldehyde	75-07-0	44	5.2	0.211	107	N	0.126	64	N	50
1-Propene, 2-methyl-	115-11-7	56	6.4	0.163	65	N	nd	nd		
Propanal	123-38-6	58	8.0	0.436	169	N	0.233	90	N	61
3-Buten-2-one	78-94-4	70	11.9	0.143	46	N	nd	nd		
Butanal	123-72-8	72	12.3	3.823	1189	N	1.932	601	N	66
1,3-Propanediol, dinitrate	3457-90-7	166	13.9	0.134	18	N	nd	nd		
Unknown			14.6	0.956	f		0.418	f		78
Nitric acid, propyl ester	627-13-4	105	19.2	0.762	162	N	0.261	56	N	98
Nitric acid, butyl ester	928-45-0	119	24.7	0.263	49	N	nd	nd		
Butane, 1-nitro-	627-05-4	103	25.1	2.065	449	N	0.538	117	N	117
Unknown C10 Alkene/Cycloalkane			33.3	0.418	f		0.207	f		67
Unknown C10 Alkene/Cycloalkane			34.0	0.176	f		nd	nd		
Cyclohexane, 1,4-dimethyl-	589-90-2	112	34.2	0.279	56	N	nd	nd		
Unknown C10 Alkene/Cycloalkane			35.4	0.182	f		nd	nd		
Unknown C11 Alkane			35.6	1.763	f		0.746	f		81
Unknown Alkane			36.1	0.232	f		nd	nd		
Unknown C11 Alkene/Cycloalkane			36.3	0.574	f		0.239	f		82
Unknown C10 Alkene/Cycloalkane			36.4	nd	nd		0.269	f		
Unknown C11 Alkene/Cycloalkane			36.7	0.344	f		nd	nd		
Unknown C11 Alkane			37.0	0.641	f		0.279	f		79
Unknown C11 Alkane			37.2	nd	nd		0.202	f		
Decane, 4-methyl-	2847-72-5	156	37.2	0.693	100	N	nd	nd		
Unknown C11 Alkane			37.3	nd	nd		0.299	f		
Unknown C11 Alkane			37.3	0.901	f		nd	nd		
Unknown C11 Alkene/Cycloalkane			37.4	0.500	f		0.204	f		84
Unknown C11 Alkane			37.6	0.785	f		0.350	f		77
Naphthalene, decahydro-, trans-	493-02-7	138	37.9	1.228	199	N	0.574	93	N	73
Unknown C11 Alkene/Cycloalkane			38.1	nd	nd		0.260	f		
Bicyclo[4.1.0]heptan-3-one, 4,7,7-trimet	4176-04-9	152	38.2	0.583	86	N	nd	nd		
Unknown Alkene/Cycloalkane			38.6	1.471	f		nd	nd		
Unknown C12 Alkene/Cycloalkane			38.7	0.617	f		nd	nd		
Unknown C11 Alkene/Cycloalkane			39.3	2.307	f		0.929	f		85
Unknown C11 Alkane			39.6	nd	nd		0.963	f		
Unknown C12 Alkane			39.6	2.440	f		nd	nd		
Unknown Cycloalkene			39.9	1.355	f		0.488	f		94
Unknown C12 Alkane			40.0	2.158	f		0.764	f		95
Naphthalene, decahydro-2-methyl-	2958-76-1	152	40.3	nd	nd		1.066	157	N	
Naphthalene, decahydro,methyl-	2958-76-1	152	40.3	2.833	418	N	nd	nd		
Cyclohexane, pentyl-	4292-92-6	154	40.8	2.856	415	N	0.991	144	N	97
Naphthalene, decahydro-2-methyl-	2958-76-1	152	41.1	5.511	812	N	1.870	276	N	99
Unknown C12 Alkane			41.3	1.482	f		nd	nd		
Unknown C13 Alkene/Cycloalkane			41.3	nd	nd		0.476	f		
Unknown C12 Alkane			41.4	4.372	f		1.440	f		101
Undecane, 3-methyl-	1002-43-3	170	41.7	2.072	273	N	nd	nd		
Unknown C12 Alkane			41.7	nd	nd		0.651	f		
Unknown C12 Alkene/Cycloalkane			42.1	0.688	f		0.253	f		93
Unknown C12 Alkene/Cycloalkane			42.5	1.948	f		nd	nd		

Table D.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis on a Single SUMMATM Canister Collected from the Headspace of Tank C-204 on 7/2/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6067-A05.153 ^(c) ISVS					Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag
Unknown			42.5	nd	nd		0.676	f	
Unknown C12 Alkene/Cycloalkane			43.0	0.477	f		0.407	f	16
Naphthalene, decahydro-2,3-dimethyl- Unknown Cycloalkane	1008-80-6	166	43.2	3.071	414	N	nd	nd	
Unknown C13 Alkane			43.2	nd	nd		0.904	f	
Unknown			43.4	19.890	f		nd	nd	
Unknown			43.4	nd	nd		6.924	f	
Unknown C12 Alkene/Cycloalkane			43.7	nd	nd		0.819	f	
Naphthalene, decahydro-2,6-dimethyl- Unknown	1618-22-0	166	44.0	1.538	208	N	nd	nd	
Unknown			44.0	nd	nd		0.824	f	
Unknown			44.0	3.111	f		nd	nd	
Unknown Alkyl Decahydronaphthalene			44.4	nd	nd		0.937	f	
1-Octadecanol	112-92-5	270	44.8	11.575	960	N	nd	nd	
Unknown			44.8	nd	nd		3.383	f	
Unknown			45.0	0.739	f		nd	nd	
Unknown C13 Alkene/Cycloalkane			45.2	3.237	f		0.897	f	113
Unknown Alkane			45.5	nd	nd		0.638	f	
Unknown Alkane			45.5	2.441	f		nd	nd	
Unknown C14 Alkane			45.7	20.796	f		6.356	f	106
Unknown Alkene/Cycloalkane			46.1	1.698	f		0.509	f	108
Unknown C13 Alkene/Cycloalkane			46.7	1.492	f		0.379	f	119
Unknown C14 Alkene/Cycloalkane			46.9	2.754	f		0.827	f	108
Unknown C14 Alkane			47.3	2.669	f		0.851	f	103
Unknown C14 Alkene/Cycloalkane			47.5	nd	nd		0.481	f	
(7E,9E)-Dodecadienal		180	47.7	0.538	67	N	nd	nd	
Unknown C14 Alkene/Cycloalkane			48.3	1.310	f		0.385	f	109
Unknown C14 Alkene/Cycloalkane			48.5	1.176	f		0.369	f	104
Unknown C13 Alkene/Cycloalkane			48.6	2.266	f		0.699	f	106
Unknown Alkane			48.8	1.152	f		0.321	f	113
Unknown C14 Alkane			49.1	0.553	f		nd	nd	
Unknown C15 Alkane			49.4	7.050	f		2.081	f	109
Bicyclo[4.1.0]heptane, 2-methyl-7-pentyl	55937-92-3	180	49.6	1.276	159	N	nd	nd	
Unknown Alkene/Cycloalkane			49.6	nd	nd		0.369	f	
Cyclohexane, 1,1,3-trimethyl-2-(3-methyl	54965-05-8	210	50.7	0.821	88	N	nd	nd	
Unknown C16 Alkane			52.2	1.391	f		nd	nd	
Unknown Alkane			52.2	nd	nd		0.460	f	
Pentadecane	629-62-9	212	53.3	0.204	22	N	nd	nd	

Data Quality Flags

B Compound found in associated laboratory blank.

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

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

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

* Flag denotes diluted value used in table

Footnotes

(a) Detected target analytes.

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

(c) WHC sample identification number.

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

nd Not detected

Table D.4. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) in Ambient Air and Ambient Air Through the ISVS Collected Near Tank C-204 in SUMMATM Canisters on 7/2/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6067-A01.126 ^(c) ISVS			S6067-A02.166 ^(c) ISVS		
				Ambient Air		Flag	Bundle Air		Flag
				(mg/m ³)	(ppbv)		(mg/m ³)	(ppbv)	
Dichlorodifluoromethane	75-71-8	121	4.6	0.007	1.3	J	0.007	1.4	J
Chloromethane	74-87-3	50	5.0	0.005	2.1	J	0.003	1.1	J
Methanol	67-56-1	32	5.3	0.234	163	Y	< 0.110	< 77	Y
Butane	106-97-8	58	5.9	0.008	3.2	J	0.002	0.92	U
Ethanol	64-17-5	46	6.9	0.150	73	Y	< 0.110	< 53	Y
Acetonitrile	75-05-8	41	7.4	0.018	9.8	J	0.004	2.2	U
Acetone	67-64-1	58	7.9	0.316	122		0.081	31	
Trichlorofluoromethane	75-69-4	137	8.3	0.005	0.78	U	0.007	1.1	J
Methylene Chloride	75-09-2	85	9.7	0.023	6.0	B	0.026	6.8	B
1,1,2-trichloro-2,2,2-trifluoroethane	76-13-1	187	10.2	0.004	0.48	U	0.394	47	
Propanol	71-23-8	60	10.9	0.020	7.3	J	0.005	2.0	J
2-Butanone	78-93-3	72	12.5	0.060	19		0.011	3.3	J
Hexane	110-54-3	86	13.8	0.004	0.98	J	0.003	0.83	U
Tetrahydrofuran	109-99-9	72	14.7	0.006	1.7	J	0.002	0.50	U
Butanenitrile	109-74-0	69	15.8	0.007	2.3	J	0.003	1.1	U
1-Butanol	71-36-3	74	16.3	0.107	32		0.009	2.8	J
Benzene	71-43-2	78	16.8	0.010	2.8	J	0.002	0.59	J
Cyclohexane	110-82-7	84	17.3	0.007	2.0	J	0.004	1.0	J
Heptane	142-82-5	100	19.3	0.005	1.1	J	0.003	0.57	J
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.010	2.1	J	0.003	0.76	U
Pyridine	110-86-1	79	20.7	0.027	7.5	J	0.019	5.3	U
Pentanenitrile	110-59-8	83	21.6	0.005	1.3	J	0.004	1.1	U
Toluene	108-88-3	92	22.6	0.070	17		0.021	5.1	
Hexanenitrile	628-73-9	97	27.1	0.006	1.5	J	0.005	1.2	U
Ethylbenzene	100-41-4	106	27.7	0.003	0.59	U	0.005	1.0	J
p/m-Xylene	106-42-3	106	28.1	0.013	2.7	U	0.014	3.0	J
Cyclohexanone	108-94-1	98	28.6	0.011	2.6	J	0.013	3.0	J
Styrene	100-42-5	104	29.1	0.005	1.2	J	0.005	1.1	J
o-Xylene	95-47-6	106	29.4	0.003	0.59	U	0.005	1.2	J
Nonane	111-84-2	128	29.8	0.005	0.93	J	0.002	0.31	U
1,3,5-Trimethylbenzene	108-67-8	120	33.0	0.002	0.37	J	0.002	0.34	U
Decane	124-18-5	142	34.5	0.010	1.6	J	0.008	1.2	J
1,3-Dichlorobenzene	541-73-1	147	34.8	0.002	0.36	J	0.002	0.27	U
1,4-Dichlorobenzene	106-46-7	147	35.0	0.003	0.47	J	0.002	0.27	U
1,2-Dichlorobenzene	95-50-1	147	36.1	0.004	0.53	J	0.002	0.27	U
Undecane	1120-21-4	156	38.8	0.009	1.3	J	0.003	0.37	U
1,2,4-Trichlorobenzene	120-82-1	181	42.3	0.005	0.61	J	0.003	0.35	U
Tridecane	629-50-5	184	46.5	0.007	0.79	J	0.056	6.8	J
Tetradecane	629-59-4	198	50.0	0.004	0.47	U	0.020	2.3	J

Tentatively Identified Compounds^(b)

Acetaldehyde	75-07-0	44	5.2	0.130	66	N	nd	nd
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Data Quality Flags

B Compound found in associated laboratory blank.

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

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

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

Footnotes

(a) Detected target analytes.

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

(c) WHC sample identification number.

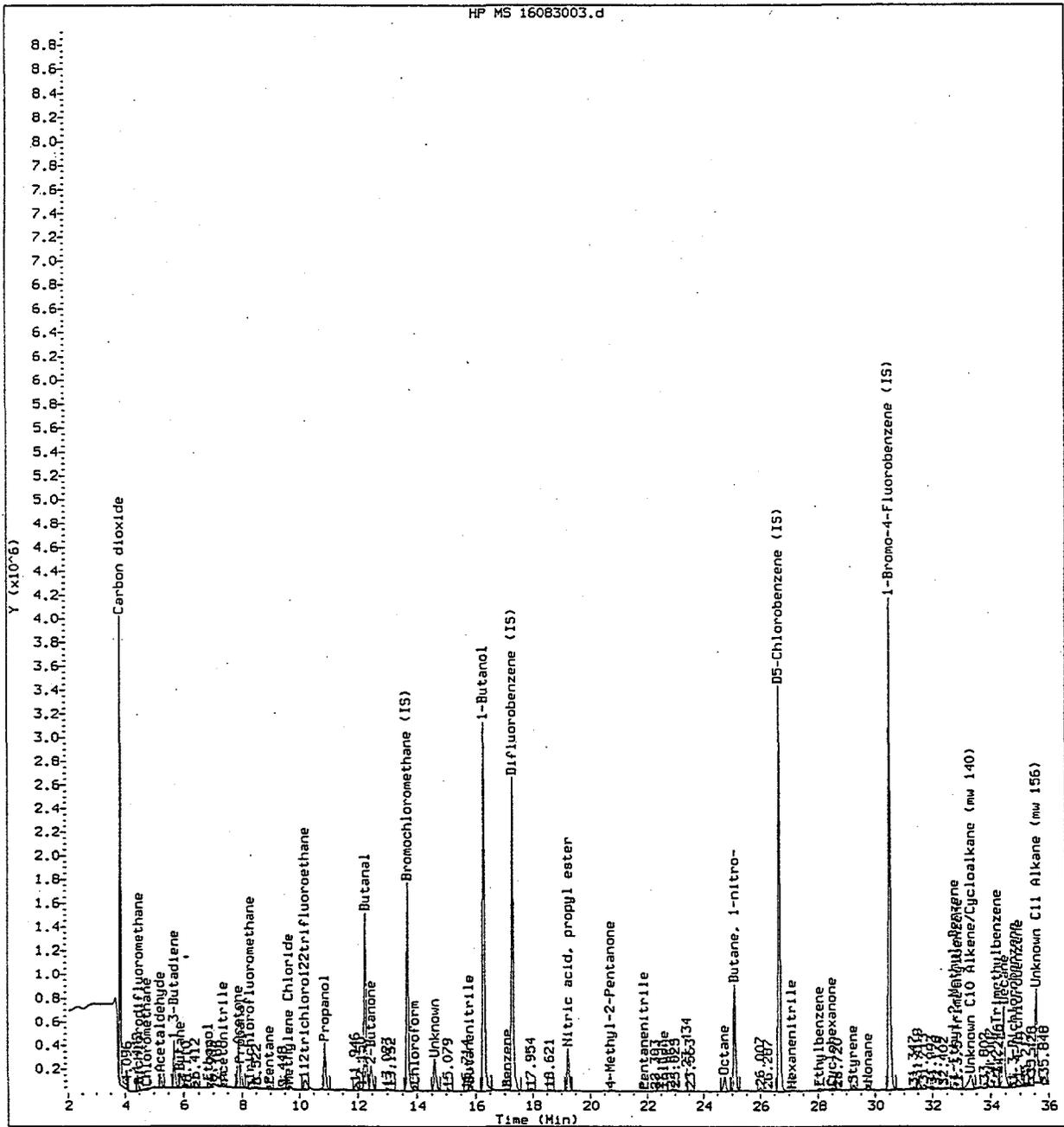


Figure D.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank C-204
SUMMA™ Canister Sample S6067-A05-153 Collected on 7/2/96

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 67 compounds. These 67 compounds that are directly quantified in this analysis make up the target analyte list (these 67 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table 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

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
Tributyl Phosphate	Methanol ^(a)
Butane	Ethanol ^(a)
<i>Acetone</i>	Pentane
1-Butanol	Pentanenitrile
Octane	Hexanenitrile
Nonane	2-Ethyl-2-methyl benzene
Undecane	Dodecane
Tridecane	Tetradecane
1,3-Butadiene ^(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.

from 100 mL to 1200 mL, and a response factor for each compound was calculated. Volumes of 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 have been determined. Methanol, ethanol, and 1,3-butadiene are not currently included in procedure PNL-TVP-10; however, these analytes 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.

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 67 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 Organic Sample Results

Eight triple sorbent traps consisting of 4 samples, 2 field blanks and 2 trip blanks were returned to the laboratory on July 10, 1996 under WHC COC form 100248. Samples were analyzed on September 4 and 5, 1996.

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

Table E.2 lists the quantitative results for compounds listed as target analytes and TICs. Target compounds not listed in Table E.2 were not detected in any of the tank headspace samples above the compound IDL. Thirty-four target analytes above the IDL and 52 TICs were detected in the tank headspace samples. Thirty-three of the target analytes and 48 TIC were observed in two or more sorbent traps. Forty-one TICs were identified and labelled as unknowns. All of these unknowns were associated with NPH compounds. Dodecane at 2.60 mg/m³ and tridecane at 2.32 mg/m³ accounted for 50% of the target analytes and 13% of the total concentration identified by the analysis. The total concentration of the target analytes was 9.88 mg/m³ or 27% of the total concentration identified by the analyses. The predominant TICs observed in these samples were an unknown C14 alkane at 4.14 mg/m³ and an unknown C13 alkane at 3.78 mg/m³. The total concentration of the TICs was 27.00 mg/m³ or 73% of the total concentration identified by analysis. The total concentration of all the compounds identified was 36.84 mg/m³.

Triple sorbent trap sample PNL 1078 was analyzed in replicate for target analytes and TICs to determine analytical precision. Eighteen of 32 target compounds and 32 of 45 TICs had RPDs of less than 10%.

The following procedural changes and observations were noted during the analysis of Tank C-204:

Methanol, ethanol, and 1,3-butadiene are not currently included in procedure PNL-TVP-10; however, these analytes 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.

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 quantitated according to the current analytical method and quality assurance program because of non-confirmation of calibration acceptability. The compound, however, was positively identified by mass spectral data.

The field blanks were relatively clean for this run showing very little effect from environmental contamination during sampling, which has been a problem on many of the past ISVS jobs. The field blanks contained a few target compounds at levels in excess of the EQL including acetone, hexane, heptane, and toluene. A number of additional compounds were detected in at least one of the blanks at trace levels (below EQL). No target compounds were present at levels above the EQL in either of the trip blanks.

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.

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

Batch 9/4/96:

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

The CCV showed acceptable performance as specified in the procedure for all target compounds except chloromethane (27%), 1,2-dichloro-1,1,2,2-tetrafluoroethane (36%),

1,3-butadiene (60%), butane (34%), acetone (30%), propanol (28%), decane (32%), and tetradecane (50%). Internal standard (IS) responses were acceptable for all six runs in the batch. Surrogate recoveries ranged from 94% to 102%. The CCB was clean of all target and TIC compounds.

Batch 9/5/96:

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

The first CCV run was deemed unsatisfactory, and a second CCV was run and used for quantitation. The second CCV was within nominal limits for all compounds except 1,2-dichloro-1,1,2,2-tetrafluoroethane (40%), 1,3 butadiene (63%), butane (42%) and acetone (26%). Internal standard responses were satisfactory for all six runs in this batch. Surrogate recoveries ranged from 87% to 105%. The CCB contained no target compounds above the EQL. Traces of methylene chloride and tetradecane (below EQL) were observed in the CCB.

The samples contained numerous target compounds at levels in excess of the EQL including butane, acetone, propanenitrile, propanol, 2-butanone, hexane, butanenitrile, 1-butanol, heptane, toluene, decane, undecane, dodecane, tridecane, and tetradecane. A number of other target compounds were detected in at least one of the samples at trace levels (below EQL). All target analytes were detected at levels below the UQL. The total ion chromatogram for these samples showed a typical NPH pattern with a large hydrocarbon hump and numerous straight chain and branched alkanes and alkenes with carbon numbers ranging from C11 to C15 resolvable above the baseline. Pentadecane was readily observable in all three samples. Other tentatively identified compounds worth noting include butanal, propyl nitrate, and nitrobutane.

Of particular interest in this sampling job was the positive identification of TBP, which had not been observed previously in any ISVS jobs. The amount of TBP observed was very low and can be considered to be below the quantitation limit estimated from the low level standard.

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.

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 C-204 on 7/2/96

Target Analytes ^(a)	CAS	MW	Ret Time (mg/m ³)	S6067-A11.1077 ^(c) ISVS		S6067-A12.1078 ^(c) ISVS		S6067-A13.1079 ^(c) ISVS		Mean and Standard Deviation			
				(ppbv)	Flag	(mg/m ³)	Flag	(mg/m ³)	Flag	(mg/m ³)	St. Dev.	(ppbv)	St. Dev.
Butane	106-97-8	58	10.8	0.106	41	0.095	37	0.094	36	0.098	0.007	38	2.6
Acetonitrile	75-05-8	41	13.1	0.025	14	0.022	12	0.019	10	0.022	0.003	12	1.7
Acetone	67-64-1	58	13.7	0.260	100	0.243	94	0.144	55	0.216	0.063	83	24
Trichlorofluoromethane	75-69-4	137	14.2	0.015	2.4	0.014	2.2	0.014	2.4	0.014	0.001	2.3	0.099
Pentane	109-66-0	72	14.9	0.020	6.2	0.018	5.6	0.023	7.0	0.020	0.002	6.3	0.70
Methylene Chloride	75-09-2	85	15.8	0.080	21	0.042	11	0.035	9.1	0.052	0.024	14	6.4
1,1,2-trichloro-2,2,2-trifluoroethane	76-13-1	187	16.3	0.012	1.5	0.003	0.38	0.004	0.51	0.008	e	0.99	e
Propanenitrile	107-12-0	55	17.0	0.028	11	0.019	7.8	0.018	7.2	0.021	0.005	8.7	2.1
Propanol	71-23-8	60	17.1	0.288	107	0.243	91	0.235	87	0.255	0.029	95	11
2-Butanone	78-93-3	72	18.6	0.105	33	0.101	31	0.097	30	0.101	0.004	31	1.3
Hexane	110-54-3	86	19.9	0.023	6.0	0.023	5.9	0.024	6.3	0.023	0.001	6.1	0.18
Tetrahydrofuran	109-99-9	72	20.8	0.020	6.2	0.021	6.6	0.019	6.0	0.020	0.001	6.3	0.32
Butanenitrile	109-74-0	69	21.9	0.214	69	0.139	45	0.116	37	0.156	0.051	51	17
1-Butanol	71-36-3	74	22.3	1.969	596	1.893	573	1.696	514	1.853	0.141	561	43
Benzene	71-43-2	78	22.8	0.008	2.2	0.007	1.9	0.007	2.0	0.007	0.000	2.0	0.14
Heptane	142-82-5	100	25.2	0.032	7.1	0.038	8.5	0.034	7.6	0.035	0.003	7.7	0.69
4-Methyl-2-Pentanone	108-10-1	100	26.4	0.009	2.0	0.017	3.9	0.017	3.8	0.014	0.005	3.2	1.1
Toluene	108-88-3	92	28.5	0.121	29	0.124	30	0.167	41	0.137	0.026	33	6.3
Octane	111-65-9	114	30.5	0.010	1.9	0.013	2.6	0.012	2.3	0.011	0.002	2.3	0.32
Ethylbenzene	100-41-4	106	33.5	0.007	1.5	0.009	1.8	0.012	2.5	0.009	0.002	2.0	0.51
p/m-Xylene	106-42-3	106	33.9	0.024	5.0	0.027	5.8	0.039	8.2	0.030	0.008	6.3	1.6
Styrene	100-42-5	104	34.8	0.008	1.7	0.009	1.9	0.012	2.6	0.010	0.002	2.1	0.51
o-Xylene	95-47-6	106	35.1	0.008	1.6	0.008	1.7	0.011	2.4	0.009	0.002	1.9	0.43
Nonane	111-84-2	128	35.5	0.011	1.9	0.012	2.0	0.008	1.5	0.010	0.002	1.8	0.29
1-Ethyl-2-methyl benzene	611-14-3	120	38.5	0.003	0.57	0.004	0.70	0.004	0.82	0.004	0.001	0.70	0.13
1,2,4-Trimethylbenzene	95-63-6	120	39.9	0.008	1.5	0.008	1.6	0.009	1.7	0.009	0.001	1.6	0.12
Decane	124-18-5	142	40.1	0.107	17	0.105	17	0.055	8.6	0.089	0.030	14	4.7
Undecane	1120-21-4	156	44.4	0.815	117	0.793	114	0.345	50	0.651	0.265	94	38
Dodecane	112-40-3	170	48.5	3.237	427	3.133	413	1.426	188	2.599	1.017	342	134
Tridecane	629-50-5	184	52.2	2.856	348	2.793	340	1.322	161	2.324	0.868	283	106
Tetradecane	629-59-4	198	55.7	1.178	133	1.103	125	0.563	64	0.948	0.335	107	38
Tributyl Phosphate	126-73-8	266	63.1	0.024	2.0	0.061	5.2	0.019	1.6	0.035	0.023	2.9	2.0

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 C-204 on 7/2/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time (mg/m ³)	S6067-A11.1077 ^(c) ISVS		S6067-A12.1078 ^(c) ISVS		S6067-A13.1079 ^(c) ISVS		Mean and Standard Deviation						
				(ppbv)	Flag	(mg/m ³)	Flag	(mg/m ³)	Flag	(mg/m ³)	St. Dev. (ppbv)	St. Dev.				
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.684	153	N	0.294	66	N	0.172	38	N	0.383	0.268	86	60
1-Propene, 2-methyl-	115-11-7	56	10.4	0.266	107	N	0.284	114	N	0.273	109	N	0.275	0.009	110	3.6
1-Butene	106-98-9	56	10.4	0.025	10	N	0.034	13	N	0.025	10	N	0.028	0.005	11	1.9
Propanal	123-38-6	58	13.8	0.064	25	N	0.071	28	N	0.075	29	N	0.070	0.006	27	2.2
2-Propanol, 2-methyl-	75-65-0	74	15.5	0.020	6.2	N	0.016	4.7	N	0.035	11	N	0.024	0.010	7.2	3.0
Butanal	123-72-8	72	18.4	0.277	86	N	0.248	77	N	0.178	55	N	0.234	0.051	73	16
2-Butenal	4170-30-3	70	21.2	0.018	5.7	N	0.016	5.0	N	0.015	4.7	N	0.016	0.002	5.1	0.52
Nitric acid, propyl ester	627-13-4	105	25.2	0.100	21	N	0.114	24	N	0.095	20	N	0.103	0.010	22	2.1
Cyclohexane, methyl-	108-87-2	98	26.7	0.100	23	N	0.103	23	N	0.097	22	N	0.100	0.003	23	0.63
Butane, 1-nitro-	627-05-4	103	30.9	0.096	21	N	0.137	30	N	0.130	28	N	0.121	0.022	26	4.8
Unknown C11 Alkane		156	41.2	0.312	45	N	0.304	44	N	nd	nd		0.308	e	44	e
Unknown C11 Alkane		156	43.0	0.183	26	N	0.184	26	N	nd	nd		0.183	e	26	e
Unknown C11 Alkane		156	43.3	0.202	29	N	0.212	30	N	nd	nd		0.207	e	30	e
Unknown C11 Alkene/Cycloalkane		154	44.2	0.224	33	N	0.250	36	N	nd	nd		0.237	e	35	e
Unknown C11 Alkene/Cycloalkane		154	44.6	0.253	37	N	0.266	39	N	nd	nd		0.259	e	38	e
Unknown C11 Alkene/Cycloalkane		154	45.0	0.455	66	N	0.461	67	N	nd	nd		0.458	e	67	e
Unknown C12 Alkane		170	45.2	0.356	47	N	0.362	48	N	nd	nd		0.359	e	47	e
Unknown C12 Alkane		170	45.7	0.543	72	N	0.559	74	N	0.261	34	N	0.454	0.168	60	22
Unknown Alkyl Decahydronaphthalene		152	46.1	0.444	65	N	0.423	62	N	nd	nd		0.434	e	64	e
Unknown C11 Alkene/Cycloalkane		154	46.5	0.732	106	N	0.748	109	N	0.323	47	N	0.601	0.241	87	35
Unknown C12 Alkane		170	46.7	0.684	90	N	0.709	93	N	0.291	38	N	0.561	0.235	74	31
Unknown Alkyl Decahydronaphthalene		152	46.9	0.835	123	N	0.844	124	N	0.351	52	N	0.676	0.282	100	42
Unknown C11 Alkane		156	47.1	0.825	118	N	0.825	118	N	0.379	54	N	0.676	0.257	97	37
Unknown C11 Alkane		156	47.4	0.542	78	N	0.542	78	N	0.256	37	N	0.447	0.165	64	24
Unknown C12 Alkene/Cycloalkane		168	48.2	0.739	99	N	0.745	99	N	0.333	44	N	0.605	0.236	81	31
Unknown C13 Alkene/Cycloalkane		182	48.7	0.315	39	N	0.336	41	N	0.147	18	N	0.266	0.104	33	13
Unknown Alkyl Decahydronaphthalene		180	49.0	0.578	72	N	0.544	68	N	0.213	26	N	0.445	0.202	55	25
Unknown C13 Alkane		184	49.1	4.525	551	N	4.546	553	N	2.259	275	N	3.777	1.314	460	160
Unknown C13 Alkene/Cycloalkane		182	49.3	0.234	29	N	nd	nd		nd	nd		e	e	e	e
Unknown C12 Alkane		170	49.4	0.436	57	N	nd	nd		0.218	29	N	0.327	e	43	e
Unknown C13 Alkene/Cycloalkane		182	50.2	0.531	65	N	0.506	62	N	0.254	31	N	0.430	0.153	53	19
Unknown C13 Alkene/Cycloalkane		182	50.5	2.144	264	N	2.146	264	N	0.980	121	N	1.757	0.672	216	83
Unknown C12 Alkene/Cycloalkane		168	50.8	0.370	49	N	0.635	85	N	0.295	39	N	0.433	0.179	58	24

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 C-204 on 7/2/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time (mg/m ³)	S6067-A11.1077 ^(c) ISVS		S6067-A12.1078 ^(c) ISVS		S6067-A13.1079 ^(c) ISVS		Mean and Standard Deviation						
				(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	St. Dev. (ppbv)	St. Dev.		
Unknown C12 Alkene/Cycloalkane		168	50.9	0.778	104	N	0.887	118	N	0.418	56	N	0.694	0.245	93	33
Unknown C13 Alkane		184	51.2	0.531	65	N	0.530	65	N	0.268	33	N	0.443	0.151	54	18
Unknown C14 Alkane		198	51.3	4.978	563	N	5.027	569	N	2.404	272	N	4.137	1.500	468	170
Unknown C14 Alkane		198	51.6	0.250	28	N	0.255	29	N	nd	nd	nd	0.252	e	29	e
Unknown C13 Alkene/Cycloalkane		182	51.8	0.275	34	N	0.248	30	N	nd	nd	nd	0.261	e	32	e
Unknown C13 Alkene/Cycloalkane		182	52.4	0.309	38	N	0.302	37	N	nd	nd	nd	0.305	e	38	e
Unknown C14 Alkene/Cycloalkane		196	52.6	0.843	96	N	0.843	96	N	0.408	47	N	0.698	0.251	80	29
Unknown C14 Alkane		198	53.0	0.661	75	N	0.660	75	N	0.323	37	N	0.548	0.195	62	22
Unknown C14 Alkene/Cycloalkane		196	53.2	0.206	23	N	0.214	24	N	nd	nd	nd	0.210	e	24	e
Unknown C13 Alkane		184	53.5	0.196	24	N	nd	nd	N	nd	nd	nd	e	e	24	e
Unknown C13 Alkene/Cycloalkane		182	54.4	0.663	82	N	0.667	82	N	0.513	63	N	0.614	0.088	76	11
Unknown C13 Alkane		184	54.5	0.338	41	N	0.299	36	N	nd	nd	nd	0.318	e	39	e
Unknown C14 Alkane		198	54.8	0.189	21	N	0.184	21	N	nd	nd	nd	0.186	e	21	e
Unknown C15 Alkane		212	55.1	2.279	241	N	2.229	236	N	1.126	119	N	1.878	0.652	198	69
Unknown C15 Alkene/Cycloalkane		210	55.4	0.252	27	N	0.216	23	N	nd	nd	nd	0.234	e	25	e
Unknown C15 Alkane		212	55.9	nd	nd	nd	0.241	26	N	nd	nd	nd	e	e	26	e
Unknown C15 Alkene/Cycloalkane		210	56.5	0.285	30	N	0.300	32	N	nd	nd	nd	0.292	e	31	e
Unknown C15 Alkane		212	57.9	0.783	83	N	0.761	80	N	0.357	38	N	0.634	0.240	67	25
Pentadecane	629-62-9	212	59.0	0.325	34	N	nd	nd	nd	nd	nd	nd	e	e	e	e

Data Quality Flags

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

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

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 C-204 on 7/2/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6067-A12.1078 ^(c) ISVS						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Butane	106-97-8	58	10.8	0.095	37		0.087	34		9
Acetonitrile	75-05-8	41	13.1	0.022	12	J	0.022	12	J	2
Acetone	67-64-1	58	13.7	0.243	94		0.184	71		28
Trichlorofluoromethane	75-69-4	137	14.2	0.014	2.2	J	0.013	2.1	J	5
Pentane	109-66-0	72	14.9	0.018	5.6	J	0.016	5.1	J	9
Methylene Chloride	75-09-2	85	15.8	0.042	11	J	0.048	13	J	13
Propanenitrile	107-12-0	55	17.0	0.019	7.8	J	0.018	7.2	J	8
Propanol	71-23-8	60	17.1	0.243	91		0.220	82		10
2-Butanone	78-93-3	72	18.6	0.101	31		0.090	28		12
Hexane	110-54-3	86	19.9	0.023	5.9		0.021	5.4		9
Tetrahydrofuran	109-99-9	72	20.8	0.021	6.6	J	0.019	5.9	J	12
Butanenitrile	109-74-0	69	21.9	0.139	45		0.146	47		5
1-Butanol	71-36-3	74	22.3	1.893	573		1.669	505		13
Benzene	71-43-2	78	22.8	0.007	1.9	J	0.007	2.1	J	10
Heptane	142-82-5	100	25.2	0.038	8.5		0.035	7.7		9
4-Methyl-2-Pentanone	108-10-1	100	26.4	0.017	3.9	J	0.013	2.9	J	30
Toluene	108-88-3	92	28.5	0.124	30		0.115	28		8
Octane	111-65-9	114	30.5	0.013	2.6	J	0.012	2.4	J	8
Ethylbenzene	100-41-4	106	33.5	0.009	1.8	J	0.008	1.7	J	5
p/m-Xylene	106-42-3	106	33.9	0.027	5.8	J	0.027	5.7	J	1
Styrene	100-42-5	104	34.8	0.009	1.9	J	0.008	1.8	J	6
o-Xylene	95-47-6	106	35.1	0.008	1.7	J	0.008	1.6	J	6
Nonane	111-84-2	128	35.5	0.012	2.0	J	0.010	1.8	J	12
1-Ethyl-2-methyl benzene	611-14-3	120	38.5	0.004	0.70	J	0.003	0.61	J	14
1,2,4-Trimethylbenzene	95-63-6	120	39.9	0.008	1.6	J	0.008	1.4	J	10
Decane	124-18-5	142	40.1	0.105	17		0.098	15		8
Undecane	1120-21-4	156	44.4	0.793	114		0.719	103		10
Dodecane	112-40-3	170	48.5	3.133	413		2.930	386		7
Tridecane	629-50-5	184	52.2	2.793	340		2.598	316		7
Tetradecane	629-59-4	198	55.7	1.103	125		1.024	116		7
Tributyl Phosphate	126-73-8	266	63.1	0.061	5.2	J	0.013	1.1	J	131
Tentatively Identified Compounds^(b)										
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.294	66	N	0.226	51	N	26
1-Propene, 2-methyl-	115-11-7	56	10.4	0.284	114	N	nd	nd		
1-Butene	106-98-9	56	10.4	0.034	13	N	0.267	107	N	155
Propanal	123-38-6	58	13.8	0.071	28	N	0.019	7.5	N	115
2-Propanol, 2-methyl-	75-65-0	74	15.5	0.016	4.7	N	0.013	4.0	N	16
Butanal	123-72-8	72	18.4	0.248	77	N	0.162	50	N	42
2-Butenal	4170-30-3	70	21.2	0.016	5.0	N	0.017	5.3	N	6
Nitric acid, propyl ester	627-13-4	105	25.2	0.114	24	N	0.094	20	N	20
Cyclohexane, methyl-	108-87-2	98	26.7	0.103	23	N	0.096	22	N	7
Butane, 1-nitro-	627-05-4	103	30.9	0.137	30	N	0.116	25	N	17
Unknown C11 Alkane		156	41.2	0.304	44	N	0.272	39	N	11
Unknown C11 Alkane		156	43.0	0.184	26	N	0.174	25	N	5
Unknown C11 Alkane		156	43.3	0.212	30	N	0.190	27	N	11
Unknown C11 Alkene/Cycloalkane		154	44.2	0.250	36	N	0.247	36	N	1
Unknown C11 Alkene/Cycloalkane		154	44.6	0.266	39	N	0.245	36	N	8

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 C-204 on 7/2/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6067-A12.1078 ^(c) ISVS						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Unknown C11 Alkene/Cycloalkane		154	45.0	0.461	67	N	0.399	58	N	14
Unknown C12 Alkane		170	45.2	0.362	48	N	0.335	44	N	8
Unknown C12 Alkane		170	45.7	0.559	74	N	0.530	70	N	5
Unknown Alkyl Decahydronaphthalene		152	46.1	0.423	62	N	0.428	63	N	1
Unknown C11 Alkene/Cycloalkane		154	46.5	0.748	109	N	0.684	100	N	9
Unknown C12 Alkane		170	46.7	0.709	93	N	0.659	87	N	7
Unknown Alkyl Decahydronaphthalene		152	46.9	0.844	124	N	0.773	114	N	9
Unknown C11 Alkane		156	47.1	0.825	118	N	0.776	111	N	6
Unknown C11 Alkane		156	47.4	0.542	78	N	0.505	73	N	7
Unknown C12 Alkene/Cycloalkane		168	48.2	0.745	99	N	0.681	91	N	9
Unknown C13 Alkene/Cycloalkane		182	48.7	0.336	41	N	0.299	37	N	12
Unknown Alkyl Decahydronaphthalene		180	49.0	0.544	68	N	0.530	66	N	3
Unknown C13 Alkane		184	49.1	4.546	553	N	4.265	519	N	6
Unknown C13 Alkene/Cycloalkane		182	49.3	nd	nd		0.247	30	N	
Unknown C12 Alkane (mw 170)		170	49.4	nd	nd		0.381	50	N	
Unknown C13 Alkene/Cycloalkane		182	50.2	0.506	62	N	0.476	59	N	6
Unknown C13 Alkene/Cycloalkane		182	50.5	2.146	264	N	2.043	251	N	5
Unknown C12 Alkene/Cycloalkane		168	50.8	0.635	85	N	0.601	80	N	6
Unknown C12 Alkene/Cycloalkane		168	50.9	0.887	118	N	0.875	117	N	1
Unknown Alkyl Decahydronaphthalene		182	51.1	nd	nd		0.175	21	N	
Unknown C13 Alkane		184	51.2	0.530	65	N	0.549	67	N	4
Unknown C14 Alkane		198	51.3	5.027	569	N	4.716	533	N	6
Unknown C14 Alkane		198	51.6	0.255	29	N	nd	nd		
Unknown C13 Alkene/Cycloalkane		182	51.8	0.248	30	N	0.273	34	N	10
Unknown C13 Alkene/Cycloalkane		182	52.4	0.302	37	N	0.275	34	N	9
Unknown C14 Alkene/Cycloalkane		196	52.6	0.843	96	N	0.770	88	N	9
Unknown C14 Alkane		198	53.0	0.660	75	N	0.614	69	N	7
Unknown C14 Alkene/Cycloalkane		196	53.2	0.214	24	N	0.206	24	N	4
Unknown C13 Alkane		184	53.5	nd	nd		0.178	22	N	
Unknown C13 Alkene/Cycloalkane		182	54.4	0.667	82	N	0.640	79	N	4
Unknown C13 Alkane		184	54.5	0.299	36	N	0.312	38	N	4
Unknown C14 Alkane		198	54.8	0.184	21	N	0.172	19	N	7
Unknown C15 Alkane		212	55.1	2.229	236	N	2.107	223	N	6
Unknown C15 Alkene/Cycloalkane		210	55.4	0.216	23	N	nd	nd		
Unknown C15 Alkane		212	55.9	0.241	26	N	0.208	22	N	15
Unknown C15 Alkene/Cycloalkane		210	56.5	0.300	32	N	0.292	31	N	3
Unknown C15 Alkane		212	57.9	0.761	80	N	0.698	74	N	9

Data Quality Flags

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

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

Footnotes

(a) Detected target analytes.

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

(c) WHC sample identification number.

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

nd Not detected

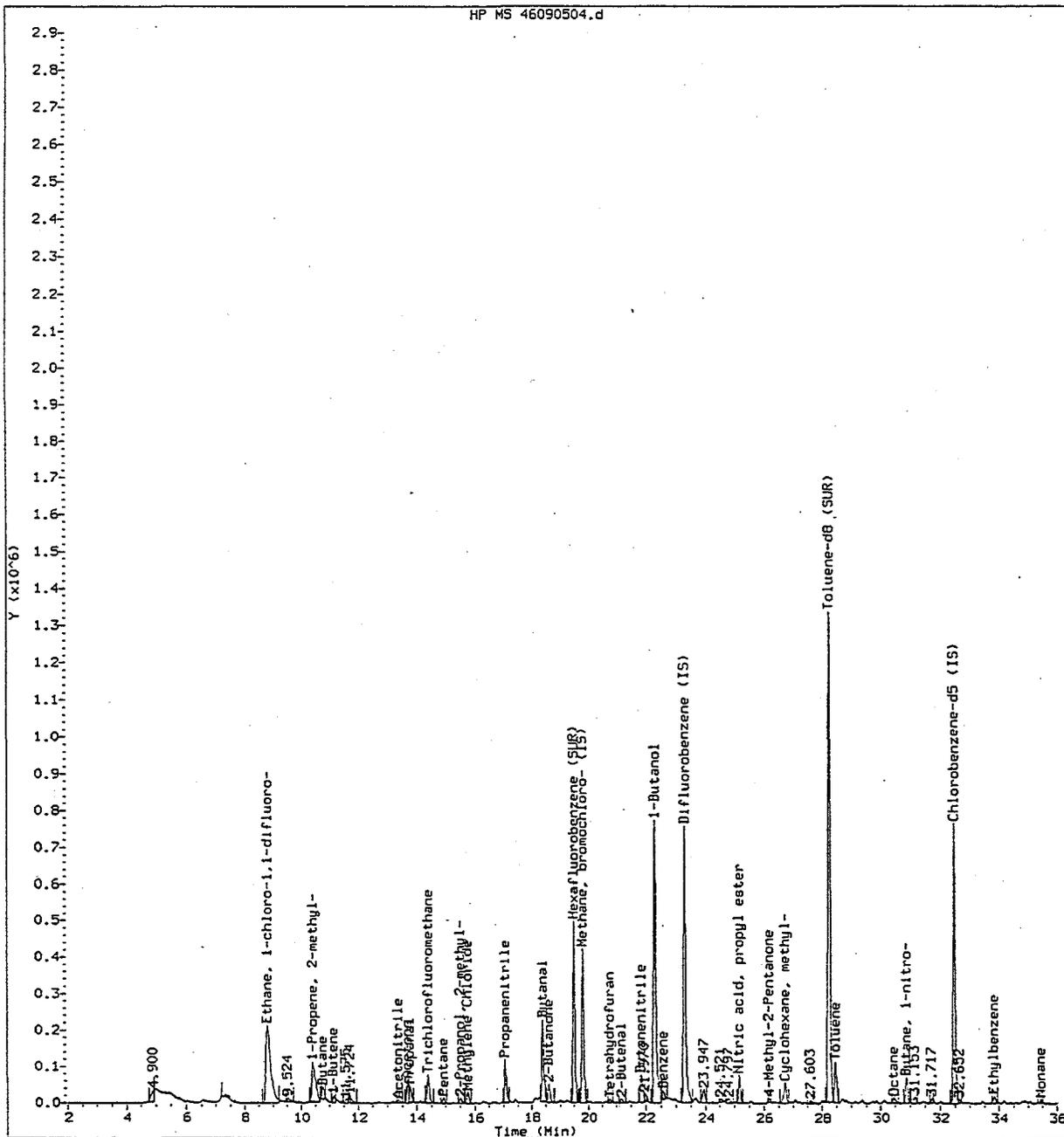


Figure E.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank C-204 Triple Sorbent Trap Sample S6067-A11-1077 Collected on 7/2/96

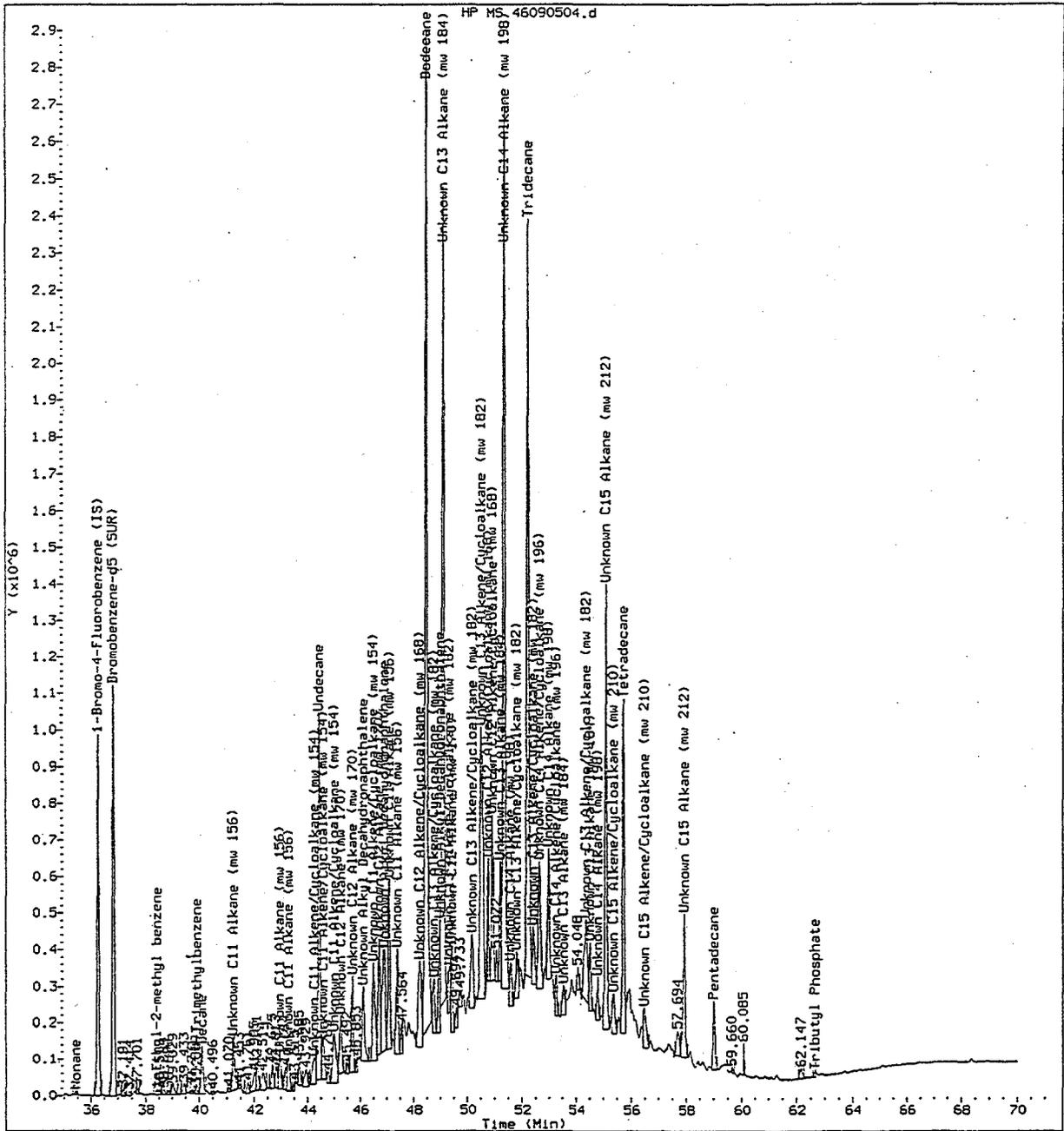


Figure E.1b Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank C-204 Triple Sorbent Trap Sample S6067-A11-1077 Collected on 7/2/96

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
241-C-204 Tank Vapor Sample SAF S6067
(ISVS Cart)

Collection date 07/07/96 06 - 2 - 96
Preparation date 06 - 17 - 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

S6067 - A07 . 22R Collect NH₃/NO_x/H₂O Sorbent Trap
S6066 - A08 . 23R Collect NH₃/NO_x/H₂O Sorbent Trap
S6067 - A09 . 24R Collect NH₃/NO_x/H₂O Sorbent Trap
S6067 - A10 . 25R Collect NH₃/NO_x/H₂O Sorbent Trap

S6067 - A15 . 26R Open, close and store NH₃/NO_x/H₂O field blank #1
S6067 - A16 . 27R 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 J.A.W. Dennis	06-20-96	1150	J A Edwards J.A. Edwards	06-20-96	1150	
J A Edwards J.A. Edwards	06-27/01/96	1055	GS CAPRIO J.D. Caprio	06-27/01/96	1055	
GS CAPRIO J.D. Caprio	07-10-96	1435	J A EDWARDS J.A. Edwards	7-10-96	1435	
J A EDWARDS J.A. Edwards	7-11-96	1400	G.W. Dennis J.A.W. Dennis	7-11-96	1400	
G.W. Dennis J.A.W. Dennis	7-17-96	1245	K.H. Pool K.H. Pool	7-17-96	1245	

Final Sample Disposition

Comments:

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

POC (Signature) POC (Signature)

Method 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 Collection date 07 - 2 - 96
241-C-204 Tank Vapor Sample SAF S6067 Preparation date 06 - 26 - 96
(ISVS Cart)

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

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

Method of Shipment Government Truck

Shipped to PNNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6067 - A01 . 126 Collect Ambient Air Sample SUMMA #1 *pos 3*
S6067 - A02 . 166 Collect Ambient Air Sample SUMMA #2 (through tube bundle) *pos 4*

S6067 - A04 . 136 Collect SUMMA #3 *pos 6*
S6067 - A05 . 153 Collect SUMMA #4 *pos 7*
S6067 - A06 . 184 Collect SUMMA #5 *pos 8*

[] 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>	07-01-96	1055	<i>Blum (L) - (S. CAPRIO)</i>	07-01-96	1055
<i>BS Caprio M Call</i>	07-10-96	1425	<i>J A Edwards</i>	7-10-96	1425

Final Sample Disposition

Comments:

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

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

Company Contact **R. D. Mahon - WHC** Telephone (509) 373-7437
 Page 85-9656 / S3-27 / FAX 373-7076

Project Designation/Sampling Locations **200 West Tank Farm**
241-C-204 Tank Vapor Sample SAF S6067
(ISVS Cart) Collection date **07 - 2 - 96**
 Preparation date **06 - 22 - 96**

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

Erteco Hi/Lo thermometer No. **PNL-T-003**

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

Method of Shipment **Government Truck**

Shipped to **WHC-**

Possible Sample Hazards/Remarks **Unknown at time of sampling**

Sample Identification

S6067 - A11 . 1077 . PNL Triple Sorbent Trap (TST) Sample # 1
 S6067 - A12 . 1078 . PNL TST Sample # 2
 S6067 - A13 . 1079 . PNL TST Sample # 3
 S6067 - A14 . 1080 . PNL TST Sample # 4

S6067 - A17 . 1081 . Open, close & store TST Field Blank # 1
 S6067 - A18 . 1082 . Open, close & store TST Field Blank #2

S6067 - A19 . 1083 . Store TST Trip Blank #1
 S6067 - A20 . 1084 . Store TST Trip Blank #2

[] Field Transfer of Custody		[X] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
JL Julya	07-01-96	0945	JA Edwards	07-01-96	0945
JA Edwards	07-01-96	1055	RS CAPRI	07-01-96	1055
RS CAPRI	07-10-96	1430	JA Edwards	7-10-96	1430
JA Edwards	07-12-96	0815	JL Julya	07-12-96	0815

Final Sample Disposition

Comments:

- | | | |
|--|--|--|
| PNL (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 | |
| Sorbents shipped on ice? (<5°C) | <input checked="" type="checkbox"/> Y / <input type="checkbox"/> N | |
| Hi/Lo thermometer - <u>Keep upright!</u> | <input checked="" type="checkbox"/> Y / <input type="checkbox"/> N | |
| Hi/Lo thermometer | / Y / N | Cooler Temperature Status |
| Rad release stickers on samples? | / Y / N | Hi -15 °C / Lo -15 °C (pick up at PNL to WHC) |
| Activity report from 222S? | / Y / N | Hi ___ °C / Lo ___ °C (delivery at WHC from PNL) |
| COC copy for LRB, RIDS filed? | / Y / N | Hi ___ °C / Lo ___ °C (at return to PNL from WHC) |
| | POC <input checked="" type="checkbox"/> POC ___ | Hi +22 °C / Lo -8 °C (at delivery from WHC to PNL) |

(Revised 06/21/95 PNL)

Distribution List

PNNL-11264

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