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TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank 241-TY-102: Results from Samples Collected on 4/12/96

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Summary

This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-TY-102 (Tank TY-102) 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 TY-102 on 4/12/96

Category	Sample Medium	Analyte	Vapor[(a)] Concentration	Units
Inorganic Analytes[(b)]	Sorbent Traps	NH_3	4.1 ± 0.1	ppmv
		NO_2	< 0.2	ppmv
		NO	< 0.2	ppmv
		H_2O	9.8 ± 0.3	mg/L
Permanent Gases	SUMMA™ Canister	CO_2	152	ppmv
		CO	3.2 U	ppmv
		CH_4	4.3 U	ppmv
		H_2	3.1 U	ppmv
		N_2O	67	ppmv
Total Non-Methane Organic Compounds (TO-12)	SUMMA™ Canister	Non-Methane Organic Compounds	0.35	mg/m^3
Volatile Organics (TO-14)	SUMMA™ Canister		0.068	ppmv
		Trichlorofluoromethane	0.053	ppmv
		Acetone	0.022 N	ppmv
		Chlorodifluoromethane		
Semi-Volatile Organics (PNL-TVP-10)	Sorbent Traps		0.092	ppmv
		Methanol	0.073 N	ppmv
		1-Chloro-1,1,difluoroethane	0.054	ppmv
		Trichlorofluoromethane		

(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).

U Compound not detected at or above the IDL.
N Tentatively identified compound.

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Glossary

% D	% Difference
CAS	Chemical Abstracts Service
CCV	continuing calibration verification
COC	chain-of-custody
C_v	concentration by volume
DIW	deionized water
EPA	U.S. Environmental Protection Agency
GC/FID	gas chromatography/flame ionization detector
GC/MS	gas chromatograph/mass spectrometer
GC/TCD	gas chromatography/thermal conductivity detection
IC	ion chromatography
IL	impact level
IS	internal standard
MDL	method detection limit
NIST	National Institute for Standards and Technology
PNL	previous designation for Pacific Northwest Laboratory
PNNL	Pacific Northwest National Laboratory
ppbv	part per billion by volume
ppm	parts per million
ppmv	part per million by volume
QA	quality assurance
RPD	relative percent difference
RSD	relative standard deviation
SAP	sample and analysis plan
SCIC	suppressed-conductivity ion chromatography
SRM	standard reference material
STP	standard temperature and pressure
SUMMA™	stainless steel, passivated interior canister
TEA	triethanolamine
TIC	tentatively identified compound
TNMHC	total non-methane hydrocarbons
TST	triple sorbent trap
UHP	ultra high purity
VAL	Vapor Analytical Laboratory
VSS	vapor sampling system
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-TY-102 (Tank TY-102) 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 S6037. Samples were collected by WHC on April 12, 1996 using the Vapor Sampling System (VSS), a truck-based sampling method using a heated probe inserted into the tank headspace.

Sampling devices and controls provided for this job included six sorbent trains for selected inorganic analytes (four sample trains and two field blanks), five SUMMA™ canisters for permanent gases and volatile organic analytes (three samples and two ambient canisters), and eight triple sorbent traps (TSTs) for semi-volatile organic analytes (four samples, two field blanks, and two trip blanks). The samples and controls were provided to WHC on April 11, 1996. Exposed samples and controls were returned to PNNL on April 17, 1996. Samples and controls were handled, stored, and transported using chain-of-custody (COC) forms to ensure sample quality was maintained.

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

Tank headspace samples were analyzed for

- *permanent gases* using gas chromatography/thermal conductivity detection (GC/TCD)
- *total non-methane organic compounds* using cryogenic preconcentration followed by gas chromatography/flame ionization detection (GC/FID)
- *volatile organic analytes* analyses using cryogenic preconcentration followed by gas chromatograph/mass spectrometer (GC/MS)

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

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

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

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

2.0 Analytical Results

Samples obtained by WHC from the headspace of Tank TY-102 on April 12, 1996 (Sample Job S6037) 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 attached 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 4.1 ± 0.1 ppmv (NH_3), < 0.2 ppmv (NO_2), < 0.2 ppmv (NO), and 9.8 ± 0.3 mg/L (primarily H_2O). The vapor concentration results were based on four samples for NH_3, NO and vapor mass concentration, and on three samples for NO_2. All samples (100%) were successfully analyzed and used in the averages. Representative field blanks were also analyzed and used to correct data.

Results provided above are estimated to be accurate to within ± 10% (assuming negligible error in the sample volume measurements) and are within the ± 30% specified by the SAP. Measurement precision, as indicated by the relative standard deviation, was 5% for the compounds found to be present at concentrations greater than the analytical method estimated quantitation limit (EQL), and within the 25% specified by the SAP. These uncertainties were confirmed by evaluation of spikes and continuing calibration standards (NH_3 and NO^-_2) and evaluation of the variability of field blanks (H_2O). All samples were analyzed within 13 days after being collected. No deviations from standard procedures were noted. Data and additional information on samples, analyses, and results are described in Appendix A. The COC form used to control samples, 100068, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent gas analysis of Tank TY-102 can be found in Appendix B. In summary, carbon dioxide at 152 ppmv and nitrous oxide at 67 ppmv were observed in the tank headspace samples.

2.3 Total Non-Methane Organic Compounds

The complete results of the TO-12 analysis of Tank TY-102 can be found in Appendix C. In summary, the average concentration in the three tank headspace samples was 0.35 mg/m^3. This compares to 0.77 mg/m^3 for the sum of all target compounds and tentatively identified compounds (TICs) identified in the analysis of the SUMMA™ canisters.

2.4 Organic Analytes by SUMMA™ Method

The complete results of the SUMMA™ analysis of Tank TY-102 can be found in Appendix D. In summary, 13 target analytes above the IDL and four TICs were detected in the tank headspace samples. Eleven target analytes and two TICs were identified in two or more tank headspace samples. One of the TICs was an unknown. Trichlorofluoromethane at 0.42 mg/m^3 and acetone at 0.14 mg/m^3 accounted for 72% of the compounds identified in the analysis. The total concentration of the target analytes was 0.66 mg/m^3. Chlorodifluoromethane at 0.09 mg/m^3 and acetaldehyde at 0.03 mg/m^3 were the only two TICs identifed in two or more of the tank headspace samples. The total concentration of all the compounds identified was 0.77 mg/m^3. This compares to a total concentration of 0.35 mg/m^3 identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 249 was analyzed in replicate for target analytes and TICs to determine analytical precision. Two of 11 compounds had RPDs of less than 10%.

Twenty-five compounds were observed in one or both of the ambient air samples. Acetone at 43 ppbv and acetaldehyde at 26 ppbv were observed in the upwind ambient air sample.

2.5 Organic Analytes by Triple Sorbent Trap Method

The complete results of the sorbent trap analysis of Tank TY-102 can be found in Appendix E. In summary, ten target analytes above the IDL and three TICs were detected in the tank headspace samples. Nine of the target analytes and one TIC were observed in two or more sorbent traps. Trichlorofluoromethane at 0.33 mg/m^3 and acetone at 0.09 mg/m^3 accounted for 71% of the target analytes and 50% of the total concentration identified by the analyses. The total concentration of the target analytes was 0.59 mg/m^3 or 69% of the total concentration identified by the analyses. The predominant TIC observed in these samples was 1-chloro-1,1-difluoroethane at 0.26 mg/m^3. The total concentration of the TICs was 0.26 mg/m^3 or 31% of the total concentration identified by analyses. The total concentration of all the compounds identified was 0.85 mg/m^3.

Triple sorbent trap sample PNL 922 was analyzed in replicate for target analytes and TICs to determine analytical precision. Five of nine compounds 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 TY-102 collected on April 12, 1996 (Sample Job S6037). 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. 2, Westinghouse Hanford Company, Richland, Washington.

Further Reading

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

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

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

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

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

Appendix A

Tank Vapor Characterization:

Inorganic Analytes

Appendix A

Tank Vapor Characterization: Inorganic Analytes

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

A.1 Sampling Methodology

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

The type and nominal quantity of sorbent material varied by application. Sorbent traps were selected for the tank sample job and included the following products. The NH_3 sorbent traps contained carbon beads impregnated with sulfuric acid; nominally, 500 mg were contained in the primary and 250 mg in the breakthrough sections. The NH_3 was chemisorbed as ammonium sulfate [$(NH_4)_2SO_4$]. The NO_2 traps contained a zeolite impregnated with triethanolamine (TEA), with 400 mg in the primary and 200 mg in the breakthrough sections. The NO_2 was absorbed and disproportionated to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). Glass tubes containing 800 mg of an oxidant such as chromate were used to convert NO to NO_2. The converted NO was then collected as nitrite and nitrate in an NO_2 trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sections.

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[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 $\leq$ 10°C because of handling recommendations for the oxidizer tubes attached to some samples. After receipt of exposed and radiologically cleared samples from WHC and disassembly of the sorbent trains, samples were provided to the analytical laboratory at ambient temperature.

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

A.1.1 Concentration Calculations. The concentrations of target compounds in the tank headspace were determined from sample results, assuming effective sample transport to the sorbent traps. Concentration, in parts per million by volume (ppmv), was determined by dividing the mass of the compound, in µmol, by the volume of the dried tank air sampled in moles. The micromolar sample mass was determined by dividing the compound mass, in µg, by the molecular weight of the compound, in g/mol. The molar sample volume was determined, excluding water vapor, by dividing the standard sample volume (at 0°C and 760 torr), in L, by 22.4 L/mol. For example, the concentration by volume (C_v) of a 3.00-L sample containing 75.0 µg of NH_3 equals

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

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

A.2 Analytical Procedures

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

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

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

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

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

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

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

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

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

A.3 Quality Assurance/Quality Control

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

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

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

Analyte	Formula	Procedure	EQL[(b)] (μg)	EQL[(b)] (ppmv)	Notification Level[(c)] (ppmv)
Ammonia	NH_3	PNL-ALO-226	1.0	0.66	≥ 150
Nitrogen Dioxide	NO_2	PNL-ALO-212	0.3	0.15	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.3	0.15	≥ 50
Mass (water)[(d)]	n/a	PNL-TVP-09	0.6 mg	0.3 mg/L	n/a

(a) Analytical precision and accuracy targets for results in the expected ranges equal ± 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 TY-102 on April 12, 1996 using the VSS. The sample job designation number was S6037. Samples were prepared, submitted to WHC for the sample job, and then returned to PNNL and analyzed to provide information on the concentrations of NH_3, NO_2, NO, and mass (primarily H_2O). Samples were controlled using COC form 100068 (Appendix F). The inorganic samples and sample volume information were received from WHC on April 17, 1996. Analyses were completed on April 24, 1996 (gravimetric, 12 days elapsed), April 25, 1996 (ammonia, 13 days elapsed), and April 25, 1996 (nitrite, 13 days elapsed).

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table A.2. The types of sample trains used and the order of sorbent traps within each train are also shown in the table. For example, the sorbent train $NH_3/NO_x/H_2O$ contained an NH_3 trap at the inlet end, a NO_x series in the middle (Section A.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table A.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank-headspace concentration results (Table A.3) are based on this information, and the listed uncertainties equal plus or minus one standard deviation of the individual results from each set of samples. Percentage relative standard deviation (RSD) may be determined by dividing the standard deviation by the average result and multiplying by 100. Where analytical results from samples, corrected for blanks, were less than the EQL in Table A.1, the concentration results (Table A.3) are listed as "less-than" the EQL value. Results of control samples, such as trip blanks, field blanks, and spiked blanks, are discussed in this section. Spiked blanks, when used, were transported to the field but not opened. Spiked samples, when used, were opened in the field and used to collect tank vapors. Sample results were not corrected for the percentage recoveries of spiked blanks.

A.4.1 Ammonia Results. The concentration of NH_3 was 4.1 ± 0.1 ppmv, based on all four samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 0.36 to 0.37 μmol in front sections; blank-corrected NH_3 was not found ($\leq$ 0.01 μmol) in back sorbent sections. Blank corrections, 0.07 μmol in front and 0.04 μmol in back sections, were about 16% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of ±0%. One blank sorbent trap was spiked with 17 μmol of NH_3 and yielded a percentage recovery of 103%. One sample leachate was spiked after initial analysis with roughly the quantity of ammonia in the sample and yielded a percentage recovery of 96%. The initial and continuing calibration verification standards, using NIST-traceable material, yielded percentage recoveries of 101% (ICV) and 99, 104, and 100% (CCV) during the analytical session. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 μg/mL.

A.4.2 Nitrogen Oxides Results. The concentrations of NO_2 and NO were both < 0.15 ppmv based on three samples for NO_2 and all four samples for NO. Blank-corrected NO_2^- quantities in the sorbent traps averaged $\leq$ 0.013 μmol. One NO_2 sample was excluded due to obvious contamination. Nitrite blank levels used to correct data were 0.0052 μmol in front (four of four blanks analyzed) and 0.0035 μmol in back (one of four blanks analyzed) sorbent sections. The analyses of two samples were duplicated and yielded repeatabilities of ± 0% and ± 2.6%. Two sample leachates were spiked with 0.125 ppm NO_2^- and yielded percentage recoveries of 97, and 104%. A 4-point calibration was performed over a concentration range of 0 to 0.5 μg NO_2^- per mL in the desorbing matrix. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 μmol NO_2^- during previous sample jobs yielded percentage recoveries of 153 ± 14, 103 ± 4, 106 ± 8, and 111 ± 7%, respectively (Clauss et al. 1994; Ligotke et al. 1994).

A.4.3 Gravimetric Results. Gravimetric results yield water vapor concentrations. This is because the total mass concentration of other vapors in the headspaces of Hanford waste tanks, measured in μg/L, are typically two or three orders of magnitude less than the mg/L mass concentrations of the water vapor found in even relatively dry tanks. The water vapor mass concentration collected in the 5-trap sorbent trains was 9.8 ± 0.3 mg/L, based on dry air sample volumes (0°C and 760 torr). The result was determined from an average mass gain of 20.7 mg from all four sample trains. The blank correction applied to the results was - 1.05 mg per train, based on a mass gain of 1.05 ± 0.15 mg per two 5-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of ± 0.1 mg. Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg water was 103 ± 2% during a previous sample job (Clauss et al. 1994).

Corrected for a measured tank headspace temperature of 13.7°C and pressure of 741.3 torr, the actual water vapor mass concentration from the gravimetric results was 9.1 ± 0.4 mg/L. Also based on analytical results, the partial pressure of water vapor was 9.0 ± 0.4 torr, the relative humidity was 77 ± 3%, and the dew point was 9.5 ± 0.4°C.

Table A.2 List of PNNL Inorganic Samples, Controls, and Gravimetric Results Obtained from a a Heated Tube Inserted into the Headspace of Tank TY-102 on 4/12/96

		Sample Port and Volume Information[a]				
Sample Number	Sorbent Train Type	Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
Samples:						
S6037-A07-S49	NH3/NOx/H2O	1	200.0	10.0	2.00	0.0209
S6037-A08-S50	NH3/NOx/H2O	2	200.0	10.0	2.00	0.0211
S6037-A09-S51	NH3/NOx/H2O	3	200.0	10.0	2.00	0.0210
S6037-A10-S52	NH3/H2O/H2O	4	200.0	10.0	2.00	0.0197
Controls:						
S6037-A15-S53	NH3/NOx/H2O Field Blank	n/a[b]	n/a	n/a	n/a	0.0012
S6037-A16-S54	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	0.0009

(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 a Heated Tube Inserted into the Headspace of Tank TY-102 on 4/12/96

	Analytical Results (µmol)			Sample	Vapor(a)
Sample	Front Section	Back Section	Total(b) Blank-Corrected	Volume (L)	Concentration (ppmv)
NH_3 Samples:			0.37	2.00	4.1 ± 0.1
S6037-A07-S49	0.43	0.039	0.36	2.00	4.0
S6037-A08-S50	0.44	NA(c)	0.37	2.00	4.1
S6037-A09-S51	0.43	0.037	0.36	2.00	4.0
S6037-A10-S52	0.44	NA	0.37	2.00	4.1
NO_2 Samples:			<0.013	2.00	<0.15
S6037-A07-S49	0.0040	0.0024	<0.013	2.00	<0.15
S6037-A08-S50	0.0040	NA	<0.013	2.00	<0.15
S6037-A09-S51	0.0042	NA	<0.013	2.00	<0.15
S6037-A10-S52	0.0661 x	0.0028	0.0609 x	2.00	1.4 x
NO Samples:			<0.013	2.00	<0.15
S6037-A07-S49	0.0067	NA	<0.013	2.00	<0.15
S6037-A08-S50	0.0064	0.0023	<0.013	2.00	<0.15
S6037-A09-S51	0.0064	0.0027	<0.013	2.00	<0.15
S6037-A10-S52	0.0064	NA	<0.013	2.00	<0.15
Gravimetric Samples:			19.6 mg	2.00	9.8 ± 0.3 mg/L
S6037-A07-S49	n/a(c)	n/a	19.9	2.00	10.0
S6037-A08-S50	n/a	n/a	20.1	2.00	10.0
S6037-A09-S51	n/a	n/a	20.0	2.00	10.0
S6037-A10-S52	n/a	n/a	18.7	2.00	9.3

(a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (Table A.2). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrite. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks. Underlined values represent the average of the set of samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. Percentage RSD may be determined by dividing standard deviation by the average and multiplying the result by 100. The use of "<" is defined in Section A.4.

(b) Total blank-corrected analyte masses (nitrite for NO_2 and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The level of analytes found in blanks is described in the subsections of Section A.4.

(c) NA = not analyzed; n/a = not applicable; x = excluded from average.

A.5 References

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

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

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

Appendix B

Tank Vapor Characterization:

Permanent Gases

Appendix B

Tank Vapor Characterization: Permanent Gases

B.1 Sampling Methodology

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

B.2 Analytical Procedure

The SUMMA™ canister samples were analyzed for permanent gases according to PNNL Technical Procedure PNL-TVP-05[b] with the exceptions listed in the following text and in the quality assurance/quality control section of this report. This method was developed in-house to analyze permanent gases, defined as hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and nitrous oxide (N_2O), by gas chromatograph/thermal conductivity detection (GC/TCD). Aliquots of sampled air are drawn directly from each canister into a 5-mL gas-tight syringe and injected into a Hewlett-Packard 5890 GC/TCD fitted with a loop injector valve and a column switching valve. An aliquot of 5 mL is used so that the 1.0-mL injection loop is completely purged with sample air, ensuring that no dilution of the sample takes place within the injection loop. One set of GC conditions is used to analyze for CO, CO_2, N_2O, and CH_4 using Helium (He) as the carrier gas. A second GC analysis is performed for H_2 (using nitrogen as the carrier gas) to enhance the signal sensitivity and lower the detection limit for this analyte. The permanent gases and the derived EQLs are listed in Table B.1.

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

[b] Pacific Northwest Laboratory. 12/95. *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. 1). PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

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

Analyte	Formula	Procedure	Instrument Detection Limit (ppmv)	Estimated Quantitation Limit (ppmv)
Carbon Dioxide	CO_2	PNL-TVP-05	2.4	24
Carbon Monoxide	CO	PNL-TVP-05	3.2	32
Methane	CH_4	PNL-TVP-05	4.3	43
Hydrogen	H_2	PNL-TVP-05	3.1	31
Nitrous Oxide	N_2O	PNL-TVP-05	2.0	20

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 CO, CO_2, N_2O, and CH_4 over a range of 25 to 2100 parts per million by volume (ppmv) using standards at five different concentrations and He as a carrier gas. A similar procedure was followed for H_2, except the carrier gas was changed to N_2. An average response factor from the calculation was used for quantification of compound peak area.

Each analyte was quantitated by comparison of sample analyte peak area to the calibration plot generated for the compound. An instrument detection limit (IDL) study was conducted and performance data are presented in Table B.1. The estimated quantitation limit (EQL) for the method has also been established as 10 times the IDL. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within ± 25% of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N_2 reagent blank, an ambient-air sample collected ~10 m upwind of Tank TY-102, and the ambient air collected through the Vapor Sampling System (VSS) 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 TY-102, ambient air collected ~10 m upwind of the tank, and ambient air collected through the VSS. Samples were analyzed on May 2 and 11, 1996. Average concentrations of carbon dioxide (152 ppmv) and nitrous oxide (67 ppmv) were observed in the tank headspace. A replicate analysis was performed on SUMMA™ PNL 249; 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 TY-102 and for Ambient Air and Ambient Air Through the VSS Collected near Tank TY-102 in SUMMA (TM) Canisters on 4/12/96

			Tank Samples				
Permanent Gas Analyte	Ambient Air Upwind S6037-A01.236(a) PNL 236(b) Concentration (ppmv)	Ambient Air Through VSS S6037-A02.239(a) PNL 239(b) Concentration (ppmv)	S6037-A04.240(a) PNL 240(b) Concentration (ppmv)	S6037-A05.249(a) PNL 249(b) Concentration (ppmv)	S6037-A06.251(a) PNL251 (b) Concentration (ppmv)	S6037-A05.249(a) PNL 249 (b)(c) Concentration (ppmv)	Average Concentration Tank Samples (ppmv)
Hydrogen	3.1 U	3.1 U	3.1 U	3.1 U	3.1 U	3.1 U	3.1 U
Methane	4.3 U	4.3 U	4.3 U	4.3 U	4.3 U	4.3 U	4.3 U
Carbon Dioxide	302	307	147	154	156	154	152
Carbon Monoxide	3.2 U	3.2 U	3.2 U	3.2 U	3.2 U	3.2 U	3.2 U
Nitrous Oxide	2 U	2 U	2 U	67	68	68	68

Data Quality Flags

U Flag denotes compound not detected above listed IDL

Footnotes

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 249; results are not included in the calculation of average concentrations.

Appendix C

Tank Vapor Characterization:

Total Non-Methane Organic Compounds

Appendix C

Tank Vapor Characterization: Total Non-Methane Organic Compounds

C.1 Sampling Methodology

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

C.2 Analytical Procedure

The SUMMA™ canister samples were analyzed according to PNNL Technical Procedure PNL-TVP-08[b], which is similar to U.S. Environmental Protection Agency (EPA) compendium Method TO-12. The method detection limits in the sub mg/m^3 are required to determine total non-methane hydrocarbon (TNMOC) concentration in the tank samples.

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

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

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

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

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

C.3 Quality Assurance/Quality Control

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

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

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

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

Before the tank samples were analyzed, a diagnostic check was performed on the GC/FID instrument by running a system cleanliness procedure and an instrument continuing calibration as described in PNL-TVP-08. First, two blank volumes of Aadco purified air were analyzed to check the cleanliness of the system. This demonstrates through the analysis of a zero-air blank that the level of interference is acceptable in the analytical system. The system should be cleaned to 0.1 mg/m^3 of TNMOCs. Second, an instrument continuing calibration is run using 100-mL UHP propane analyzed using the response factor as an external standard method followed by one blank volume of Aadco air.

C.3.1 Quantitation Results of Target Analytes. The mg/m^3 was derived from the five-point multilevel calibration curve from the propane standard using the following equation:

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

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

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

C.4 Total Non-Methane Organic Compounds Sample Results

Table C.1 lists results of the TO-12 gas analysis from samples collected from the headspace of Tank TY-102, ambient air collected ~10 m upwind of the tank, and ambient air collected through the VSS. Samples were analyzed on May 9, 1996. Concentrations in the ambient air samples ranged from 0.18 mg/m^3 to 0.32 mg/m^3. Concentrations in the three tank headspace samples ranged from 0.32 mg/m^3 to 0.37 mg/m^3 with an average concentration of 0.35 mg/m^3. This compares to 0.77 mg/m^3 for the sum of all compounds identified in the target and TIC analysis of the SUMMA™ canisters.

Table C.1. TO-12 Results for Samples Collected from the Headspace of Tank TY-102 and for Ambient Air and Ambient Air Through the VSS Collected near Tank TY-102 in SUMMA™ Canisters on 04/12/96

	Ambient Air Upwind S6037-A01.236[a] PNL 236[b] Concentration (mg/m3)	Ambient Air Through VSS S6037-A02.239[a] PNL 239[b] Concentration (mg/m3)	Tank Samples				
			S6037-A04.240[a] PNL 240[b] Concentration (mg/m3)	S6037-A05.249[a] PNL 249[b] Concentration (mg/m3)	S6037-A06.251[a] PNL 251 [b] Concentration (mg/m3)	S6037-A05.249[a] PNL 249 [b][c] Concentration (mg/m3)	**Average Concentration Tank Samples (mg/m3)**
TO-12	0.32 J	0.18 J	0.35 J	0.37 J	0.32 J	0.36 J	0.35 J

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 249; results are not included in the calculation of average concentrations.

Data Qualifier Flags

J TO-12 result above the IDL, but below the EQL.

Appendix D

Tank Vapor Characterization:

Organic Analytes by SUMMA™ Method

Appendix D

Tank Vapor Characterization: Organic Analytes by SUMMA™ Method

D.1 Sampling Methodology

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

D.2 Analytical Procedure

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

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

[b] Pacific Northwest Laboratory. 2/96. *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. 1), PNL Technical Procedure, Richland, Washington.

The instrument calibration mixture for the PNL-TVP-03 analysis consists of 66 organic analytes. These 66 compounds that are directly quantified in this analysis make up the target analyte list (these 66 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table D.1. The calibration mixture was prepared by blending a commercially prepared TO-14 calibration mixture with a mixture created using a Kin-Tek® permeation-tube standard

Table D.1 Target Organic Analytes

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

(a) The low level standard is used as the EQL for these compounds generation system. The operation of the permeation-tube system follows the method detailed in PNNL Technical Procedure PNL-TVP-06(a). The standard calibration mix was analyzed using four aliquot sizes ranging from 30 mL to 200 mL, and a response factor for each compound was calculated. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. Instrument detection limits and EQLs for the target analytes have been developed.

D.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "high-sensitivity tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated using a standard gas mixture containing 66 organic compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d_5, and bromofluorobenzene was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank headspace samples are analyzed.

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

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

D.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/National Institute for Standards and Technology (NIST) and WILEY electronic mass spectra libraries. Chromatographic peaks with an area count greater than, or equal to, one-tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. This is roughly equivalent to 10 ppbv, depending on the relative response factor of the individual TIC as compared with the nearest elution IS. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

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

The concentration of each TIC was estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration in mg/m^3:

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

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

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

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

D.4 Volatile Organic Sample Results

Five SUMMA™ canisters were returned to the laboratory on April 17 under WHC COC form 100066 (see Appendix F). Samples were analyzed on July 25, 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 TY-102 and through the VSS near Tank TY-102 are presented in Table D.4.

Table D.2 lists the quantitative results for compounds listed as target analytes and TICs. Thirteen target analytes above the IDL and four TICs were detected in the tank headspace samples. Eleven target analytes and two TICs were identified in two or more tank headspace samples. One of the TICs was an unknown. Trichlorofluoromethane at 0.42 mg/m^3 and acetone at 0.14 mg/m^3 accounted for 72% of the compounds identified in the analysis. The total concentration of the target analytes was 0.67 mg/m^3. Chlorodifluormethane at 0.08 mg/m^3 and acetaldehyde at 0.03 mg/m^3 were the only two TICs identifed in two or more of the tank headspace samples. The total concentration of all the compounds identified was 0.78 mg/m^3. This compares to a total concentration of 0.35 mg/m^3 identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 249 was analyzed in replicate for target analytes and TICs to determine analytical precision. The RPD results are presented in Table D.3. The RPDs were calculated for analytes detected above the IDL and found in both replicates. Two of 11 compounds had RPDs of less than 10%.

Table D.4 lists the quantitative results for compounds listed as target analytes and TICs in ambient air and ambient air through the VSS. Twenty-five compounds were observed in one or both of the ambient air samples. Acetone at 43 ppbv and acetaldehyde at 26 ppbv were observed in the upwind ambient air sample.

The following procedural changes and observations were noted during the analysis of Tank TY-102:

Four target compounds (1,1,1-trichloroethane at 33.85%, carbon tetrachloride at 34.32%, 1,2-dichloropropane at 31.45%, and heptane at 33.04) surpassed the 30% relative standard deviation (% RSD) acceptance criteria for the initial calibration. Carbon tetrachloride was found in the S6037-A04.240, S6037-A05.249, S6037-A05.249-REP and S6037-A06.251 tank samples in concentrations between the IDL and the EQL. The compounds 1,1,1-trichloroethane, 1,2-dichloropropane and heptane were not found in the tank sample in concentrations above IDL.

Nine target compounds (acetone, 1,2-dichloroethane, hexanenitrile, cyclohexanone, 1,2,4-trichlorobenzene, dodecane, hexachloro-1,3-butadiene, tridecane and tetradecane) were outside the 25% difference (% D) acceptance criteria for the continuing calibration verification (CCV) sample; however, the CCV passed the procedural criterion requiring +25% D passage for 85% of all target compounds. Acetone was found in all the tank samples in concentrations between the EQL and the Upper quantitation limit (UQL). These concentrations may be over estimated. Tetradecane was found in tank samples S6037-A01.236, S6037-A02.239, S6037-A04.240 and S6037-A05.249 in concentrations just above the IDL. The compounds 1,2-dichloroethane, cyclohexanone, 1,2,4-trichlorobenzene, dodecane, hexachloro-1,3-butadiene and tridecane were not found in the tank samples in concentrations above the IDL.

Only one target compound, 1,2,4-trichlorobenzene, was found in the CCB above the EQL. Acetone, methylene chloride, 2-butanone, 1-butanol and 1,2,4-trichlorobenzene were detected in ICB above their EQLs.

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

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 TY-102 in SUMMA™ Canisters collected on 4/12/96

			Ret	S6037-A04.240[c]			S6037-A06.251[c]			S6037-A05.249[c][d]			Mean and Standard Deviation			
Target Analytes[a]	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	(mg/m^3	St. Dev	(ppbv)	St. Dev
Dichlorodifluoromethane	75-71-8	121	4.6	0.005	0.95	J	0.005	0.89	J	0.005	0.88	J	0.005	0.000	0.91	0.04
Methanol	67-56-1	32	5.2	< 0.110	< 77	Y	< 0.110	< 77	Y	0.120	84	Y	e	e	e	e
Acetonitrile	75-05-8	41	7.3	0.030	17	J	0.008	4.4	J	0.029	16	J	0.023	0.013	12	6.8
Acetone	67-64-1	58	7.9	0.155	60		0.109	42		0.151	58		0.138	0.026	53	9.9
Trichlorofluoromethane	75-69-4	137	8.3	0.364	59		0.423	69		0.466	76		0.418	0.052	68	8.4
Methylene Chloride	75-09-2	85	9.7	0.028	7.5		0.032	8.4		0.032	8.5		0.031	0.002	8.1	0.58
2-Butanone	78-93-3	72	12.5	0.008	2.5	J	0.006	2.0	J	0.027	8.5	J	0.014	0.012	4.3	3.62
1-Butanol	71-36-3	74	16.3	0.009	2.7	J	0.008	2.5	J	0.011	3.3	J	0.009	0.001	2.8	0.44
Benzene	71-43-2	78	16.7	0.002	0.55	J	0.002	0.57	J	0.002	0.62	J	0.002	0.000	0.58	0.04
Carbon Tetrachloride	56-23-5	154	17.0	0.006	0.86	J	0.008	1.2	J	0.007	0.96	J	0.007	0.001	1.0	0.16
Tetrachloroethylene	127-18-4	166	25.2	0.011	1.5	J	0.011	1.5	J	0.011	1.5	J	0.011	0.000	1.5	0.02
Hexanenitrile	628-73-9	97	27.1	0.005	1.2	U	0.005	1.2	J	0.005	1.2	U	e	e	e	e
Tetradecane	629-59-4	198	50.0	0.005	0.58	J	0.004	0.47	U	0.005	0.54	J	0.005	e	0.56	e
Tentatively Identified Compounds[b]																
Methane, chlorodifluoro-	75-45-6	86	4.3	0.097	25	N	0.080	21	N	0.077	20	N	0.085	0.011	22	2.8
Acetaldehyde	75-07-0	44	5.2	0.027	14	N	0.015	7.6	N	0.040	20	N	0.027	0.012	14	6.3
Unknown			7.6	nd	nd		0.056	f		nd	nd		e	e	e	e
Butanal	123-72-8	72	12.3	nd	nd		nd	nd		0.008	2.5	N	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.

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

Footnotes

(a) Detected target analytes.

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

(c) WHC sample identification number.

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

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

(f) No molecular weight available for calculation.

nd Not Detected

Table D.3. Positively Identified and Quantitated Target Analytes(a) and Tentatively Identified Compounds and Estimated Concentrations(b) of Replicate Analysis of a Single SUMMA™ Canister Collected from the Headspace of Tank TY-102 on 4/12/96

			Ret	S6037-A05.249(c)			S6037-A05.249(c)			Relative Percent Difference(d)
Target Analytes(a)	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	%
Dichlorodifluoromethane	75-71-8	121	4.6	0.005	0.9	J	0.004	0.68	J	26
Methanol	67-56-1	32	5.2	0.120	84	Y	< 0.110	< 77	Y	
Acetonitrile	75-05-8	41	7.3	0.029	16	J	0.004	2.2	U	
Acetone	67-64-1	58	7.9	0.151	58		0.121	47		22
Trichlorofluoromethane	75-69-4	137	8.3	0.466	76		0.391	64		18
Methylene Chloride	75-09-2	85	9.7	0.032	8.5		0.033	8.6		1
2-Butanone	78-93-3	72	12.5	0.027	8.5	J	0.018	5.6	J	41
1-Butanol	71-36-3	74	16.3	0.011	3.3	J	0.007	2.0	J	49
Benzene	71-43-2	78	16.7	0.002	0.62	J	0.002	0.51	J	20
Carbon Tetrachloride	56-23-5	154	17.0	0.007	1.0	J	0.008	1.2	J	18
Tetrachloroethylene	127-18-4	166	25.2	0.011	1.5	J	0.011	1.5	J	2
Tetradecane	629-59-4	198	50.0	0.005	0.54	J	0.004	0.47	U	
Tentatively Identified Compounds(b)										
Methane, chlorodifluoro-	75-45-6	86	4.3	0.077	20	N	0.063	16	N	19
Acetaldehyde	75-07-0	44	5.2	0.040	20	N	0.029	15	N	30
Butanal	123-72-8	72	12.3	0.008	2.5	N	nd	nd		

Data Quality Flags

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

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

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

Footnotes

(a) Detected target analytes.

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

(c) WHC sample identification number.

(d) Relative percent differences (RPDs) based on mg/m^3 values

nd Not Detected

Table D.4. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identified and Estimated Concentrations[b] in Ambient Air and Ambient Air Through the VSS Collected Near Tank TY-102 in SUMMA™ Canisters on 4/12/96

				Upwind Ambient S6037-A01.236[c]			Upwind Ambient Thru VSS S6037-A02.239[c]		
Target Analytes[a]	CAS	MW	Ret Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag
Dichlorodifluoromethane	75-71-8	121	4.6	0.004	0.74	J	0.006	1.2	J
Chloromethane	74-87-3	50	4.9	0.002	1.1	U	0.004	1.7	J
Acetonitrile	75-05-8	41	7.3	0.004	2.2	U	0.008	4.2	J
Acetone	67-64-1	58	7.9	0.113	43		0.057	22	
Methylene Chloride	75-09-2	85	9.7	0.035	9.3		0.030	8.0	
Propanol	71-23-8	60	10.9	0.016	6.0	J	0.003	1.0	U
2-Butanone	78-93-3	72	12.5	0.015	4.7	J	0.006	1.8	J
1-Butanol	71-36-3	74	16.3	0.021	6.5	J	0.012	3.7	J
Benzene	71-43-2	78	16.7	0.003	0.83	J	0.002	0.67	J
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.003	0.76	U	0.004	0.78	J
Pyridine	110-86-1	79	20.6	0.023	6.4	J	0.019	5.3	U
Styrene	100-42-5	104	29.0	0.003	0.63	J	0.002	0.47	U
Nonane	111-84-2	128	29.8	0.003	0.57	J	0.002	0.31	U
Decane	124-18-5	142	34.5	0.006	0.90	J	0.003	0.47	U
1,3-Dichlorobenzene	541-73-1	147	34.7	0.002	0.34	J	0.002	0.27	U
1,4-Dichlorobenzene	106-46-7	147	34.9	0.003	0.43	J	0.002	0.27	U
1,2-Dichlorobenzene	95-50-1	147	36.1	0.003	0.50	J	0.002	0.27	U
Undecane	1120-21-4	156	38.8	0.004	0.55	J	0.003	0.37	U
1,2,4-Trichlorobenzene	120-82-1	181	42.3	0.009	1.1	J	0.003	0.35	U
Tridecane	629-50-5	184	46.5	0.009	1.1	J	0.006	0.73	U
Tetradecane	629-59-4	198	50.0	0.010	1.1	J	0.006	0.72	J
Tentatively Identified Compounds[b]									
Unknown			4.8	nd	nd		0.025	d	
Acetaldehyde	75-07-0	44	5.2	0.051	26	N	0.021	11	N
Unknown Alcohol			8.3	0.005	d		nd	nd	
Unknown			10.4	0.051	d		0.046	d	
Butanal	123-72-8	72	12.3	0.012	3.6	N	nd	nd	

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) No molecular weight available for calculation.

nd Not Detected

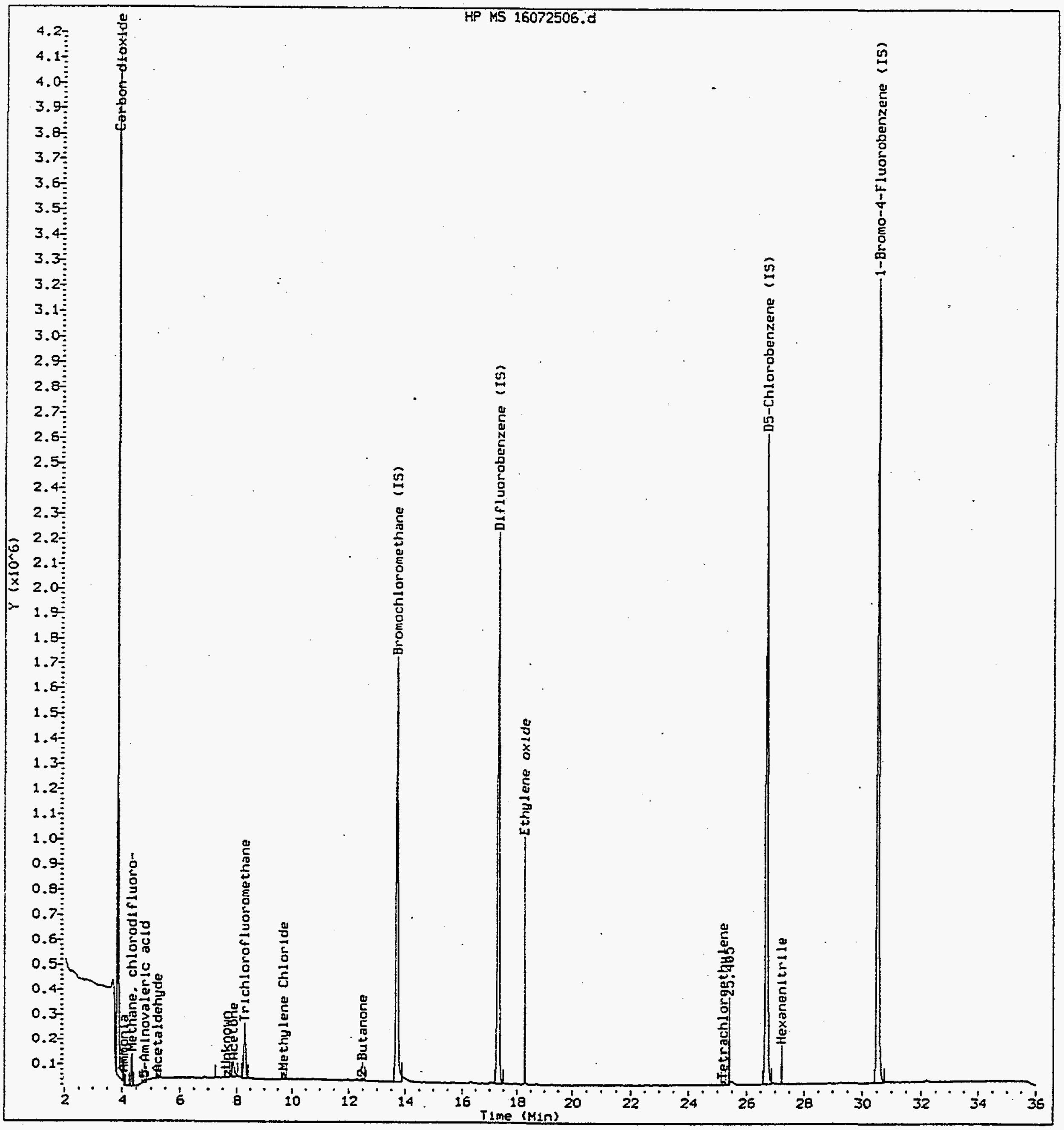

Figure D.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank TY-102 SUMMA™ Canister Sample S6037-A06-251 Collected on 4/12/96

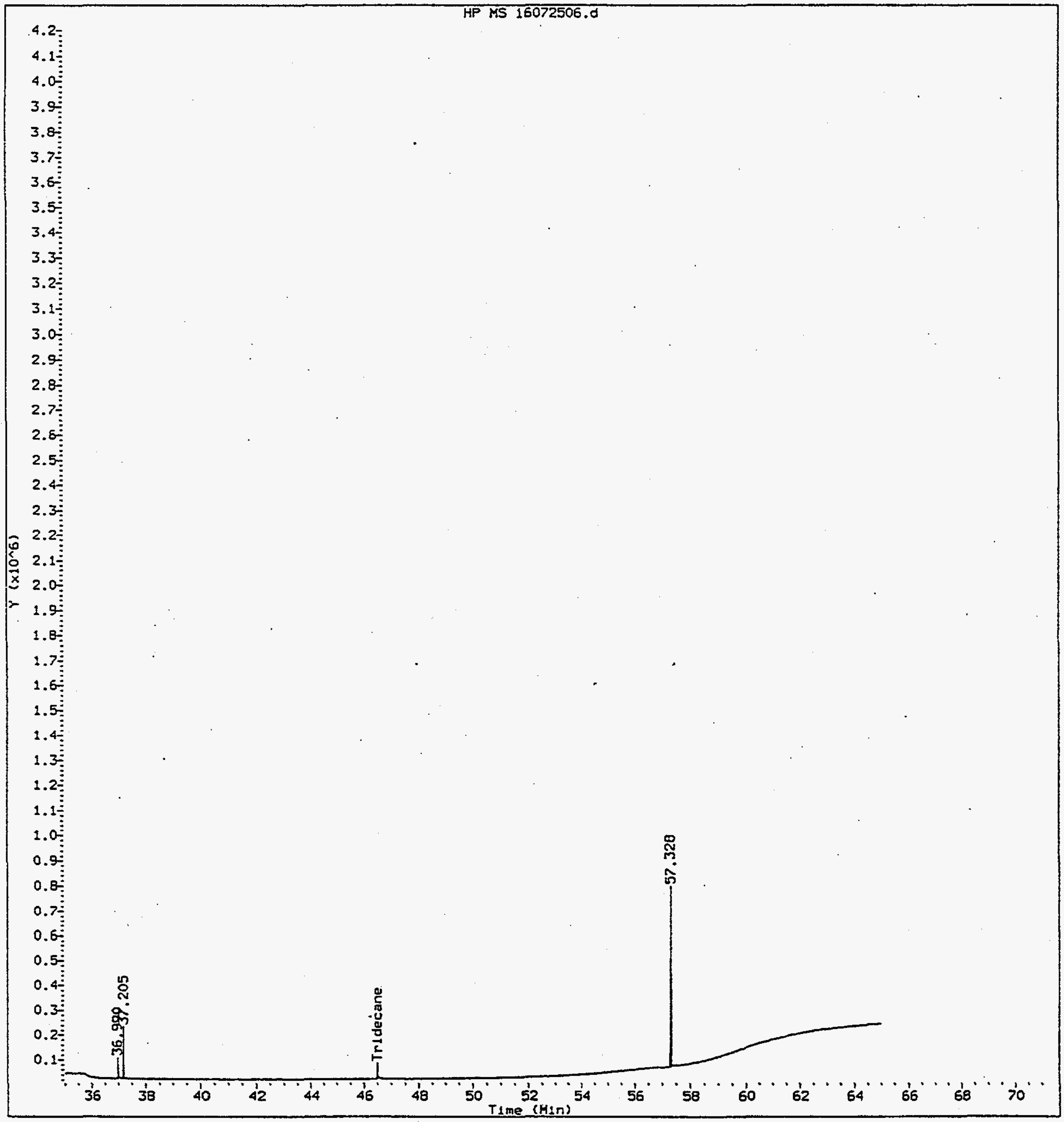

Figure D.1b Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank TY-102 SUMMA™ Canister Sample S6037-A06-251 Collected on 4/12/96

Appendix E

Tank Vapor Characterization:

Organic Analytes
by Triple Sorbent Trap Method

Appendix E

Tank Vapor Characterization: Organic Analytes by Triple Sorbent Trap Method

E.1 Sampling Methodology

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

E.2 Analytical Procedure

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

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

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

The instrument calibration mixture for the TST analysis consists of 65 compounds. These 65 compounds that are directly quantified in this analysis make up the target analyte list (these 65 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table E.1. The calibration mixture is prepared in common with the mixture used for the SUMMA™ analysis (see Section D.2). The standard calibration mix was analyzed using 4 aliquot sizes ranging from 100 mL to 1200 mL, and a response factor for each compound was calculated. Volumes of

Table E.1 Target Organic Analytes

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

(a) The low level standard is used as the EQL for these compounds.
Note: Compounds shown in italics have an exceptionally high volatility. They are routinely included in the standard and are quantified, but have a restricted linear dynamic range because of the potential for trap breakthrough.

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

E.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running a full auto tune, as described in PNL-TVP-10. Upon satisfactory completion of the instrument diagnostic check, a blank tube was analyzed to check the cleanliness of the system. The instrument was then calibrated using a 300-mL volume of standard gas mixture containing 65 compounds shown in Table E.1. A gas mixture containing difluorobenzene, chlorobenzene-d_5, and 1,4 bromofluorobenzene was used as an IS for all calibration standard and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. A continuing calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample.

E.3.1 Quantitation Results of Target Analytes. The quantitative-analysis results for the target analytes were calculated directly from the calibration curve generated using the IS method described above and in PNL-TVP-10. The second IS will be used to calculate the relative response factor for these compounds for subsequent analyses. The conversion from ppbv to mg/m^3 assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

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/m^3:

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

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

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

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

E.4 Organic Sample Results

Eight triple sorbent traps consisting of four samples, two field blanks and two trip blanks were returned to the laboratory on April 17, 1996 under WHC COC form 100067. Samples were analyzed on May 15, 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. Ten target analytes above the IDL and three TICs were detected in the tank headspace samples. Eight of the target analytes and one TIC were observed in two or more sorbent traps. Trichlorofluoromethane at 0.33 mg/m^3 and acetone at 0.09 mg/m^3 accounted for 71% of the target analytes and 50% of the total concentration identified by the analyses. The total concentration of the target analytes was 0.59 mg/m^3 or 69% of the total concentration identified by the analyses. The predominant TIC observed in these samples was 1-chloro-1,1-difluoroethane at 0.26 mg/m^3. The total concentration of the TICs was 0.26 mg/m^3 or 31% of the total concentration identified by analyses. The total concentration of all the compounds identified was 0.85 mg/m^3.

Triple sorbent trap sample PNL 922 was analyzed in replicate for target analytes and TICs to determine analytical precision. The RPD results are presented in Table E.3. The RPDs were calculated for analytes detected above the detection limit and found in both replicates. Five of nine compounds had RPDs of less than 10%.

The following procedural changes and observations were noted during the analysis of Tank TY-102:

> Methanol and ethanol are not currently included in procedure PNL-TVP-10; however, both compounds were analyzed per this method. The low level standard is used as the EQL for these compounds. Sample results are flagged with a less-than symbol (<) when less than the EQL value.
>
> Tributyl phosphate is included in the target list based on a calibration performed on January 5 and 9, 1996. The TBP was introduced onto a series of double sorbent traps as a methanolic solution standard rather than a vapor standard. This served to determine the retention time and verify the mass spectral characteristics of the compound. However, verification of the calibration acceptability was not performed because the compound is not present in the CCV. At present, it is not possible to prepare a gas standard from this material. The calibration

information on TBP demonstrated that detectability at 0.08 ppbv (based on 200 mL sample) was possible. Tributyl phosphate was not detected in the tank samples.

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

The field and trip blanks contained no compounds at levels in excess of the EQL. Compounds detected in at least one of the blanks at trace levels (below EQL) included methanol, acetone, methylene chloride, 2-butanone, 4-methyl-2-butanone, and tetradecane. Note that the trace quantities found in the blanks for methylene chloride and tetradecane were comparable to the amounts found in the system blank (CCB) and may represent false positives. Both field blanks contained minor amounts of 1-chloro-1,1-difluoroethane (TIC). This analyte was not detected in either trip blank, but was detected in the tank samples. 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. That material is never present in tubes archived for a similar amount of time in the 326 Vapor Lab or 329 Building temporary storage. The origin of the material is unclear but since it has shown up in trip blanks as well as field blanks, the most likely candidate is one of the refrigerators used for interim storage such as the 222S lab.

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

Batch 5/14/96 (file identifier 46051401.d) - S6037-A17.926, S6037-A18.927, S6037-A19.928, S6037-A20.929;

Batch 5/15/96 (file identifier 46051501.d) - S6037-A11.921, S6037-A12.922, S6037-A12.922REP, S6037-A13.923.

The following discussion provides details regarding QC criterion failures for each batch.
Batch 5/14/96:

The CCV was satisfactory for all target compounds except methanol (39.6%), ethanol (33.4%), pyridine (25.5%), tridecane (26.1%), and tetradecane (66.0%). The CCB contained trace amounts (below EQL) of methylene chloride and tetradecane.

Batch 5/15/96:

The CCV was satisfactory for all target compounds except ethanol (37.2%), pyridine (27.0%), and tetradecane (33.5%). The internal standard area response for sample 46051505 was somewhat below nominal acceptance limits; however, since that sample was a repeat run on a split tube, a lower than typical response is expected due to losses associated with the first analysis of the sample. The CCB contained trace amounts (below EQL) of methylene chloride and tetradecane. The CCB was otherwise clean.

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 TY-102 on 4/12/96

			Ret	S6037-A11.921[c]			S6037-A12.922[c][d]			S6037-A13.923[c]			Mean and Standard Deviation			
Target Analytes[a]	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	mg/m^3	(ppbv)	Flag	(mg/m^3)	stdev	(ppbv)	stdev
Methanol	67-56-1	32	10.1	< 0.274	< 192	Y	< 0.274	< 192	Y	< 0.274	< 192	Y	e	e	e	e
Acetone	67-64-1	58	13.8	0.070	27	J	0.078	30		0.119	46		0.089	0.026	34	10
Trichlorofluoromethane	75-69-4	137	14.2	0.333	54		0.327	53		0.339	55		0.333	0.006	54	1.0
Methylene Chloride	75-09-2	85	15.9	0.049	13	J	0.042	11	J	0.030	7.9	J	0.040	0.010	11	2.5
2-Butanone	78-93-3	72	18.7	0.008	2.5	J	0.012	3.7	J	0.015	4.5	J	0.012	0.003	3.6	1.0
Carbon Tetrachloride	56-23-5	154	23.2	0.012	1.7	J	0.011	1.7	J	0.012	1.8	J	0.012	0.000	1.7	0.056
4-Methyl-2-Pentanone	108-10-1	100	26.5	0.011	2.5	J	0.002	0.46	U	0.002	0.46	U	e	e	e	e
Toluene	108-88-3	92	28.6	0.002	0.55	J	0.002	0.58	J	0.002	0.58	J	0.002	0.000	0.57	0.017
Tetrachloroethylene	127-18-4	166	31.1	0.021	2.8	J	0.020	2.7	J	0.021	2.8	J	0.021	0.001	2.8	0.085
Tetradecane	629-59-4	198	55.8	0.108	12	J	0.076	8.7	J	0.064	7.2	J	0.083	0.023	9.4	2.6
Tentatively Identified Compounds[b]																
Unknown			5.0	0.103	f		nd	nd		nd	nd		e	e	e	e
Unknown			5.0	nd	nd		nd	nd		0.115	f		e	e	e	e
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.9	0.473	106	N	0.179	40	N	0.129	29	N	0.260	0.186	58	42

Data Quality Flags

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

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

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

Footnotes

(a) Detected target analytes.

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

(c) WHC sample identification number.

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

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

(f) Molecular weight not available

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 TY-102 on 4/12/96

			Ret	S6037-A12.922[c]			S6037-A12.922[c]			Relative Percent Difference[d]
Target Analytes[a]	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	%
Methanol	67-56-1	32	10.1	0.110	77	J	0.027	19	U	
Acetone	67-64-1	58	13.8	0.078	30		0.083	32		7
Trichlorofluoromethane	75-69-4	137	14.2	0.327	53		0.331	54		1
Methylene Chloride	75-09-2	85	15.9	0.042	11	J	0.080	21	J	62
2-Butanone	78-93-3	72	18.7	0.012	3.7	J	0.010	3.1	J	16
Carbon Tetrachloride	56-23-5	154	23.2	0.011	1.7	J	0.010	1.5	J	11
Toluene	108-88-3	92	28.6	0.002	0.58	J	0.003	0.60	J	4
Tetrachloroethylene	127-18-4	166	31.1	0.020	2.7	J	0.021	2.8	J	6
Tetradecane	629-59-4	198	55.8	0.076	8.7	J	0.070	7.9	J	9
Tentatively Identified Compounds[b]										
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.9	0.179	40	N	0.155	35	N	15

Data Quality Flags

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

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

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

Footnotes

(a) Detected target analytes.

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

(c) WHC sample identification number.

(d) Relative percent differences (RPDs) based on mg/m^3 values

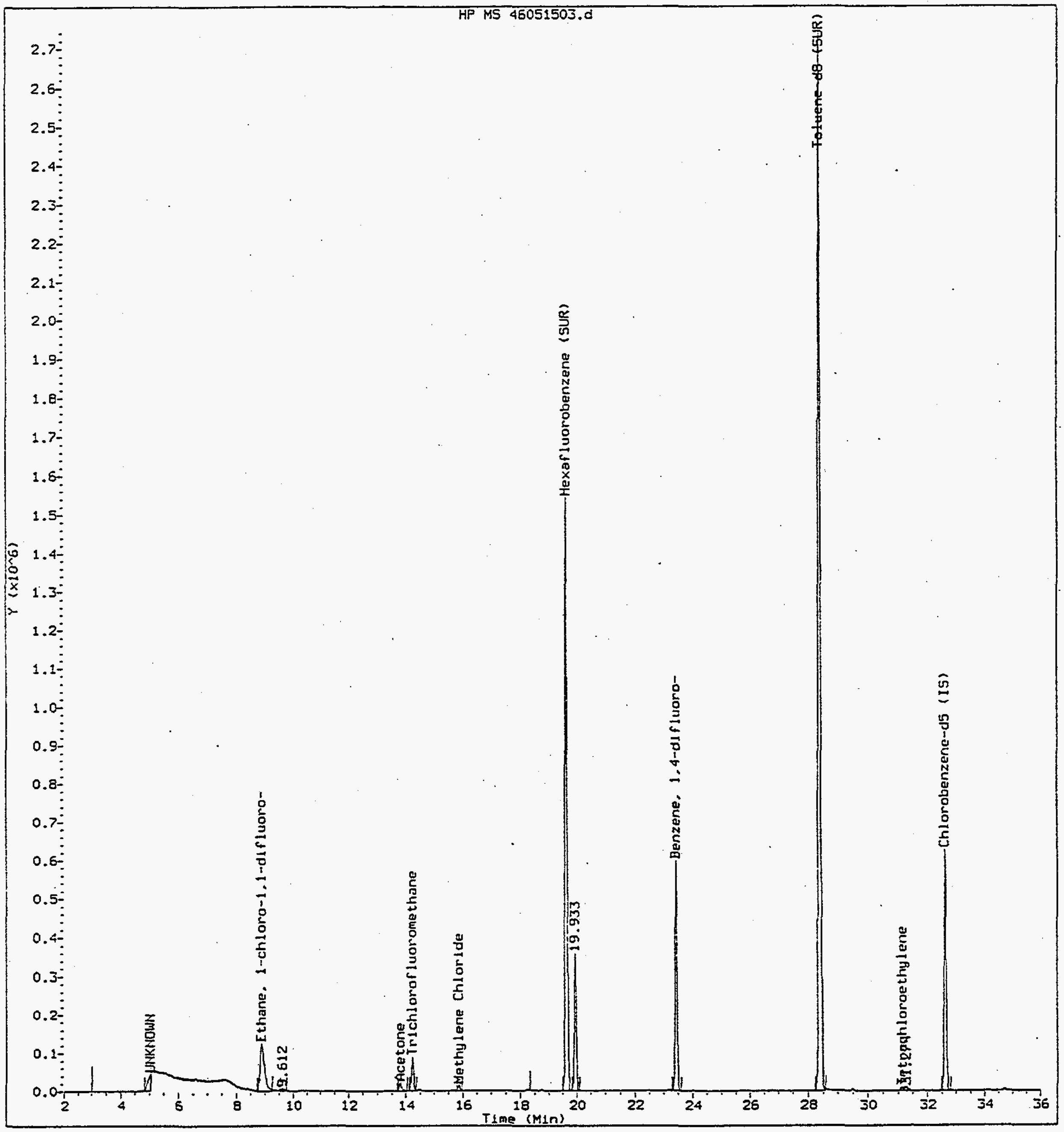

Figure E.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank TY-102 Triple Sorbent Trap Sample S6037-A11-921 Collected on 4/12/96

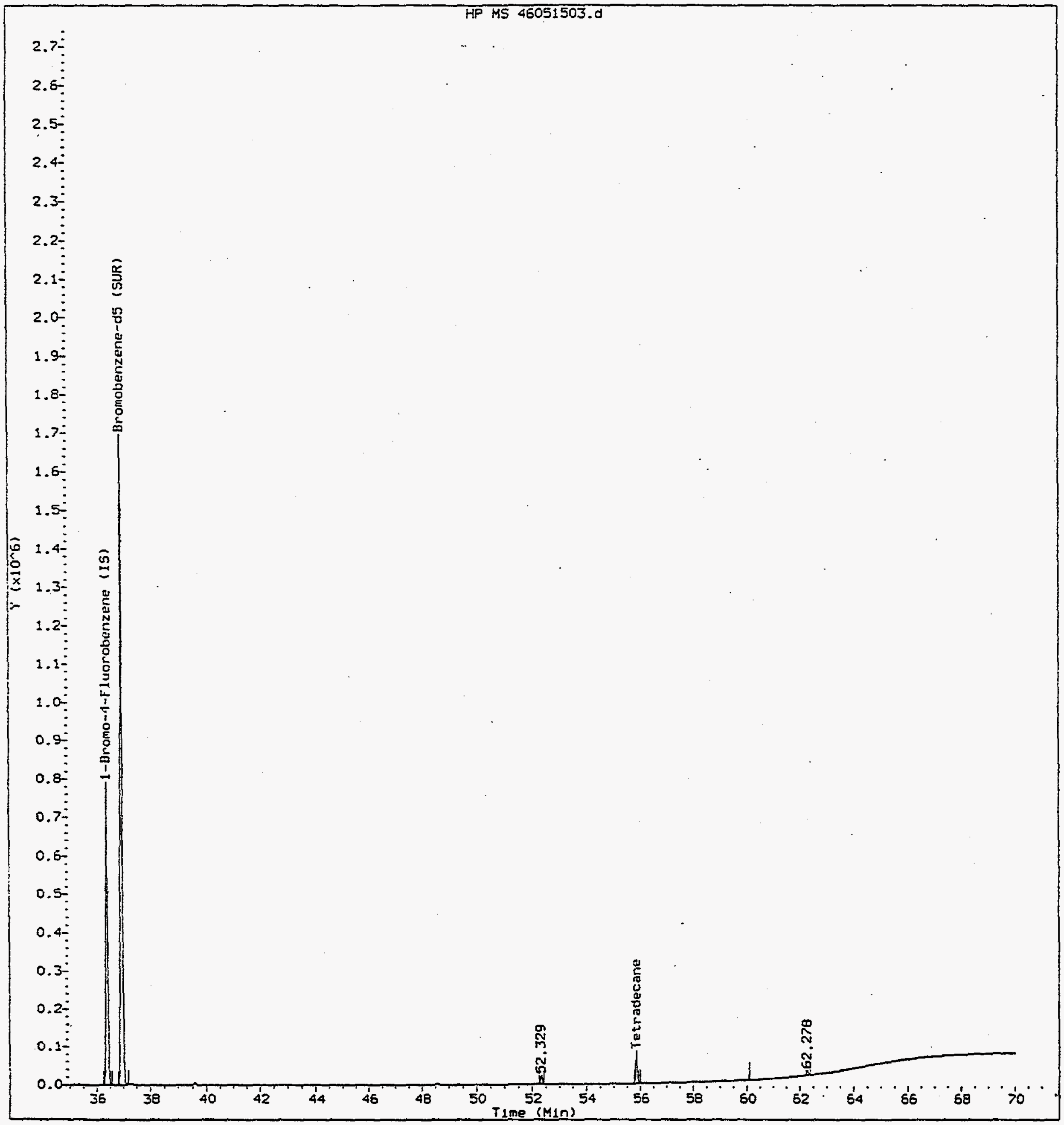

Figure E.1b Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank TY-102 Triple Sorbent Trap Sample S6037-A11-921 Collected on 4/12/96

Appendix F

Tank Vapor Characterization:

Chain of Custody Sample Control Forms

Battelle Pacific National Northwest Lab	CHAIN OF CUSTODY	WHC 100068

Custody Form Initiator J. A. Edwards - PNNL
Telephone (509) 373-0141
Page 85-3009 / FAX 376-0418

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-TY-102 Tank Vapor Sample SAF S6037
VSS
Collection date 04 - 12 - 96
Preparation date 04 - 08 - 96

Ice Chest No.
Field Logbook No. WHC-N-647 10

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

S6037 - A07 . S49	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6037 - A08 . S50	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6037 - A09 . S51	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6037 - A10 . S52	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6037 - A15 . S53	Open, close and store $NH_3/NO_x/H_2O$ field blank #1
S6037 - A16 . S54	Open, close and store $NH_3/NO_x/H_2O$ 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	04 - 10 -96	1345	J L Julya / Janet L Julya	04 - 10 -96	1345
J L Julya / Janet L Julya	04 - 11 -96	1207	T. B Utecht / T B Utecht	04 - 11 -96	1207
T.B Utecht / T B Utecht	4-17-96	1350	J A Edwards / J A Edwards	4-17-96	1350
J A Edwards / J A Edwards	4-22-96	1335	G.W. Dennis / G.W. D	4-22-96	1335
G.W.Dennis / G.W.D	4-24-96	1230	K.H. Pool / Karl Pool	4-24-96	1230

Final Sample Disposition

Comments:

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

POC POC

(Revised 11/30/95 PNNL)

A-6000-407 (12/92) WEF061

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Battelle Pacific National Northwest Lab	CHAIN OF CUSTODY	WHC 100066

Custody Form Initiator J. A. Edwards - PNNL
Telephone (509) 373-0141
Page 85-3009 / FAX 376-0418

Company Contact R. D. Mahon - WHC
Telephone (509) 373-2891
Page 85-9656 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm
241-TY-102 Tank Vapor Sample SAF S6037
(VSS Truck)
Collection date 04 - 12 - 96
Preparation date 04 - 08 - 96

Ice Chest No.
Field Logbook No. WHC-N-647-10

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

S6037 - A01 . 236	Collect Ambient Air Sample SUMMA #1	Upwind of Tank
S6037 - A02 . 239	Collect Ambient Air Sample SUMMA #2	Through VSS
S6037 - A04 . 240	Collect SUMMA #3	
S6037 - A05 . 249	Collect SUMMA #4	
S6037 - A06 . 251	Collect SUMMA #5	

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

Relinquished By	Date	Time	Received By	Date	Time
JAEDWARDS / JA Edwards	04-10-96	1445	Janet L Julya / Janet L Julya	04-10-96	1445
TBU 4-11-96 ~~T B Ulrich / T B Ulrich~~	~~4/11/96~~	~~1207~~		—	—
JL Julya / Janet L Julya	4-11-96	1207	T B Ulrich / T B Ulrich	4-11-96	1207
T B Ulrich / T B Ulrich	4-17-96	1350	JAEdwards / JA Edwards	4-17-96	1350

Final Sample Disposition

Comments:

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

POC POC

(Revised 11/30/95 PNNL)

Battelle Pacific Northwest National Laboratory	**CHAIN OF CUSTODY**	**WHC 100067**

Custody Form Initiator J. A. Edwards - PNNL
Telephone (509) 373-0141
Page 85-3009 / FAX 376-0418

Company Contact R. D. Mahon - WHC
Telephone (509) 373-2891
Page 85-3152 / FAX 373-3793

Project Designation/Sampling Locations 200 East Tank Farm
241-TY-102 Tank Vapor Sample SAF S6037
(VSS Truck)

Collection date 04 - 12 - 96
Preparation date 04 - 08 - 96

Ice Chest No.

Field Logbook No. WHC-N-647-10

Method of Shipment Government Truck

Shipped to PNNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6037 - A11 . 921	TST(Triple Sorbant Tube) Sample #1	
S6037 - A12 . 922	TST Sample #2	
S6037 - A13 . 923	TST Sample #3	
S6037 - A14 . 925	TST Sample #4	
S6037 - A17 . 926	TST Field Blank #1	Open in VSS Truck
S6037 - A18 . 927	TST Field Blank #2	Open in VSS Truck
S6037 - A19 . 928	TST Trip Blank #1	
S6037 - A20 . 929	TST Trip Blank #2	

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

Relinquished By	Date	Time	Received By	Date	Time
J.L. Julya Janet L Julya	04-10-96	0930	J A Edwards JA Edwards	04-10-96	0930
JAEDWARDS JAEdwards	04-10-96	1345	Janet L Julya (Janet L Julya)	04-10-96	1345
JLJulya / Janet L Julya	4-11-96	1207	T E [illegible] / T E [illegible]	4-11-96	1207
T E [illegible] / T E [illegible]	4-17-96	1350	JAEDWARDS / JAEdwards	4-17-96	1350
JAEDWARDS / JAEdwards	4-18-96	1110	JLJulya JL Julya	4-18-96	1110

Final Sample Disposition

Comments:

PNL (only) Checklist	Pick-up	/ Delivery
◊ Media labeled and checked?	[✓ Y] N	
◊ Media in good condition?	[✓ Y] N	/ [✓ Y] N
◊ COC info/signatures complete?	[✓ Y] N	/ [✓ Y] N
◊ Sorbents shipped on ice? (<5°C)	Y / N	/ [✓ Y] N
◊ Hi/Lo thermometer - *Keep upright!*	[✓ Y] N	
◊ Hi/Lo thermometer		/ [✓ Y] N
◊ Rad release stickers on samples?		/ ~~Y~~ [✓ N] 4/17/96
◊ Activity report from 222S?		/ [✓ Y] N
◊ COC copy for LRB, RIDS filed?	POC	/ [✓ Y] N POC

Comments:

Cooler Temperature Status #6
Hi ____°C / Lo ____°C (pick up at PNNL to WHC)
Hi ____°C / Lo ____°C (delivery at WHC from PNNL)
Hi ____°C / Lo ____°C (at return to PNNL from WHC)
Hi +6 °C / Lo -24 °C (at delivery from WHC to PNNL)

(Revised 04/10/96 PNNL)

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Distribution List

PNNL

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

Lockheed

Larry Pennington	S7-21
Luther Buckley	R2-12

DOE-RL

Carol Babel	S7-54
Jim Thompson	S7-54