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TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank SX-101: Results from Samples Collected on 7/21/95

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Summary

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

Table S.1. Summary Results of Samples to Characterize the Headspace of Tank SX-101 on 7/21/95

Category	Sample Medium	Analyte	Vapor[a] Concentration	Units
Inorganic Analytes[b]	Sorbent Traps	NH_3	3.8 ± 0.4	ppmv
		NO_2	0.10 ± 0.02	ppmv
		NO	0.13 ± 0.01	ppmv
		H_2O	11.8 ± 0.5	mg/L
Permanent Gases	SUMMA™ Canister	CO_2	338	ppmv
		CO	<25	ppmv
		CH_4	<25	ppmv
		H_2	<25	ppmv
		N_2O	<25	ppmv
Total Non-Methane Hydrocarbons (TO-12)	SUMMA™ Canister	Hydrocarbons	0.98	mg/m^3
Volatile Organics (TO-14)	SUMMA™ Canister	Methyl Alcohol	0.060	ppmv
		Acetone	0.033	ppmv
		Trichlorofluoromethane	0.023	ppmv
Semi-Volatile Organics (PNL-TVP-10)	Sorbent Traps	Acetone	0.034	ppmv
		Trichlorofluoromethane	0.024	ppmv

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

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

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Glossary

% D	% Difference
CAS	Chemical Abstracts Service
CCV	Continuing Calibration Verification
CO	carbon monoxide
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 chromatography/mass spectrometry
GC/TCD	gas chromatography/thermal conductivity detection
He	Helium
HP	Hewlett Packard
IC	ion chromatography
IL	impact level
IS	internal standard
MDL	method detection limit
NIST	National Institute for Standards and Technology
NO	nitric oxide
OGI	Oregon Graduate Institute
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
SIE	selective ion electrode
SRM	standard reference material
STP	standard temperature and pressure
SUMMA™	stainless steel, passivated interior canister
TEA	triethanolamine
TIC	tentatively identified compound
TNMOC	total nonmethanic organic compounds
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-SX-101 (Tank SX-101) at the Hanford Site in Washington State. Pacific Northwest National Laboratory (PNNL)[a] contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and analyze samples for inorganic and organic analytes collected from the tank headspace and ambient air near the tank. The analytical work was performed by the PNNL Vapor Analytical Laboratory (VAL) under 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 S5045. Samples were collected by WHC on July 21, 1995, 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 11 sorbent trains for selected inorganic analytes (8 sample trains and 3 field blanks), 5 SUMMA™ canisters for permanent gases and volatile organic analytes (3 sample and 2 ambient canisters), and 10 triple-sorbent traps (TSTs) for semi-volatile organic analytes (6 samples, 2 field blanks, and 2 trip blanks). The samples and controls were provided to WHC on July 10, 1995. Exposed samples and controls were returned to PNNL on July 27 and 28, 1995. Samples and controls were handled, stored, and transported using chain-of-custody (COC) forms to ensure that 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).

SUMMA™ canister samples were analyzed for:

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

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

(b) PNL-TVP-07, Rev. 0, October 1994, *Sample Shipping and Receiving Procedure for PNL Waste Tank Samples*, PNL Technical Procedure, Tank Vapor Project, 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 SX-101 on July 21, 1995 (Sample Job S5045) were analyzed in the PNNL VAL. 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, NO and vapor mass concentration (primarily H_2O) were determined. The average and 1 standard deviation of concentration results from inorganic sorbent sample trains used to sample headspace vapors were 3.8 $\pm$ 0.4 part per million by volume (ppmv) (NH_3), 0.10 $\pm$ 0.02 ppmv (NO_2), 0.13 $\pm$ 0.01 ppmv (NO), and 11.8 $\pm$ 0.5 mg/L (primarily H_2O). The vapor-concentration results were based on six samples for each compound (eight samples for mass concentration). The NO_2 and NO samples included four samples trailing (downstream of) NH_3 sorbent traps and two samples unprotected by NH_3 sorbent traps. All samples (100%) were successfully analyzed and used in the averages. Representative field blanks were also analyzed and used to correct data. One of the nine analyzed NO_x sample back sorbent sections was found to be contaminated and was excluded from the analysis; it was possible to exclude the contaminated back sorbent section because the level of contamination was three-fold greater than the level of nitrite found in the samples, and the contamination problem clearly did not occur with the actual samples.

Two of the 4 average concentration results exceeded the minimum of the expected ranges (see Table A.1): NH_3 and H_2O. The precision of results, based on 1 standard deviation of all samples, was $\leq \pm$ 11% (within the target level of $\pm$ 25%) for analytes exceeding expected ranges. The estimated accuracies of vapor concentrations, assuming negligible sample-volume uncertainty, were 90 to 110% (within the target range of 70 to 130%) for analytes exceeding the expected ranges. These uncertainties were confirmed by evaluating spikes and continuing calibration standards (NH_3) and evaluating the variability of field blanks (H_2O). No procedural deviations were noted. Data and additional information on samples, analyses, and results are described in Appendix A. The COC form used to control samples, 008912, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent-gas analysis of Tank SX-101 can be found in Appendix B of this report. In summary, carbon dioxide was observed above the method detection limit in the tank headspace samples. Carbon dioxide in the headspace samples was at a similar concentration observed in the ambient air.

2.3 Total Non-Methane Hydrocarbons

The complete results of the TO-12 analysis of Tank SX-101 can be found in Appendix C of this report. In summary, the average concentration in the 3 tank-headspace was 0.98 mg/m^3. This compares to 0.38 mg/m^3 for the sum of all compounds identified in the target and tentatively identified compound (TIC) analysis of the SUMMA™ canisters.

2.4 Volatile Organic Analytes

The complete results of the SUMMA™ analysis of Tank SX-101 can be found in Appendix D of this report. In summary, 3 target analytes above the 5-part per billion by volume (ppbv) reporting cutoff and 5 TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. Two target analytes and two TICs were identified in 2 or more tank headspace samples. The total concentration of the target analytes was found to be 0.23 mg/m^3. The total TICs concentration was found to be 0.15 mg/m^3. The total concentration of all the compounds identified was 0.38 mg/m^3. SUMMA™ canister PNL 58 was analyzed in replicate for target analytes and TICs to determine analytical precision. One of 2 target analytes and the 3 of 5 TICs had a relative percent difference (RPD) of less than 10%. Acetone and pyridine were 2 target analytes observed in the ambient air samples. One TIC, 3-buten-2-one, was observed in the upwind ambient air sample.

2.5 Semi-Volatile Organic Analytes

The complete results of the sorbent-trap analysis of Tank SX-101 can be found in Appendix E of this report. In summary, 4 target analytes above the 5-ppbv reporting cutoff and 3 TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. Two of 4 target analytes and none of the TICs were observed in 2 or more sorbent traps. The total concentration of the target analytes was 0.24 mg/m^3. Triple sorbent trap (TST) sample PNL 538 was analyzed in replicate for target analytes and TICs to determine analytical precision. None of the 3 target analytes nor the single TIC had RPDs of less than 10%.

2.6 Comparison of Organic Results

Table 2.1 contains a comparison of the SUMMA™ and TST analytical results for target analytes and TICs. The compounds identified in this table were observed in two or more of the tank headspace samples of the respective sampling method. Unknown compounds identified during the respective analysis were not included in this comparison. The RPD is based on comparing the TST results to the SUMMA™ results. For example, a smaller TST value would be identified as a negative RPD.

The analytical results of the SUMMA™ and TST samples identified 2 target analytes and no TICs which were common to both sampling methods. Both target analytes, acetone and trichlorofluoromethane, compared within 10% for both sampling methods.

Table 2.1. Comparison of Mean Values for Positively Identified and Quantitated Target Analytes[a] and Tentatively Identified Compounds and Estimated Concentrations[b] for Triple Sorbent Traps and SUMMA™ Canister Collected from the Headspace of Tank SX-101 on 7/21/95

Target Analytes	CAS No.	S5045[c] TST Results (mg/m^3)	St Dev	S5045[c] SUMMA™ Results (mg/m^3)	St Dev	Relative Percent Difference %
Acetone	67-64-1	0.09	0.01	0.09	0.02	0
Trichlorofluoromethane	75-69-4	0.15	0.08	0.14	0.02	7
Tentatively Identified Compounds[b]						
Methyl Alcohol	67-56-1	<0.01		0.09	0.04	na
1-Butanol	71-36-3	<0.03		0.06	0.03	na

(a) TO-14 plus 14 additonal target analytes.
(b) Semi-quantitative estimate calculated using concentration of closest eluting internal standard
(c) WHC sample job number.
na Not applicable

3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank SX-101 on July 21, 1995 (Sample Job S5045). 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 QA requirements, where significant, were documented in this report, as required by the SAP (Homi 1995). No immediate notifications (phone and electronic memo) 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. OE, Westinghouse Hanford Company, Richland, Washington.

Further Reading

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

Pacific Northwest Laboratory. *Quality Assurance Manual, Part 2: Good Practices Standard*. PNL-MA-70, Part 2, Pacific Northwest Laboratory, Richland, Washington.

Pacific Northwest Laboratory. *PNL Tank Vapor Characterization Project Quality Assurance Plan*. MCS-046, Rev. 0, Pacific Northwest Laboratory, Richland, Washington.

U.S. Department of Energy. *Hanford Analytical Services Quality Assurance Plan (HASQAP)*. DOE/RL-94-55, Rev. 2, United States 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)[a] 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 samples effectively trapped NH_3 and mass. Samples were prepared, handled, and disassembled as described in Technical Procedure PNL-TVP-09[b]. Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNNL quality assurance (QA) impact level (IL) 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 2 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, having glass-sealed ends, were received from the vendor.

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

(a) Pacific Northwest National Laboratory is operated for the U. S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

(b) Pacific Northwest Laboratory. 10/94. *Sorbent Trap Preparation for sampling and Analysis: Waste Tank Inorganic Vapor Samples*, PNL-TVP-09 (Rev.0), PNL Technical Procedure, 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 having 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 mol. The micromolar sample mass was determined by dividing the compound mass, in μg, by the molecular weight of the compound, in g/mol. The molar sample volume was determined, excluding water vapor, by dividing the standard sample volume (at 0°C and 760 torr), in L, by 22.4 L/mol. For example, the concentration by volume (C_v) of a 3.00-L sample containing 75.0 μg of NH_3 equals

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

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

A.2 Analytical Procedures

The compounds of interest were trapped using solid sorbents and chemisorption (adsorption of water vapor). Analytical results were based on extraction and analysis of selected ions. Analytical procedures used are specified in the text. All were compiled in PNL-MA-599.

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[(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 5 or 6 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). Emf 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) 1 guard column (AG4A) and 2 separator columns (AS4A) in series instead of just 1 separator column, and 3) all standards, samples, and blanks 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 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 1 of the midrange standards was performed after the analysis of every 6 samples. If the instrument response indicated that sample nitrite

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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.

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. 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. Blanks were included to provide information on uncertainty.

A.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNNL documents. The samples were analyzed following PNNL Impact Level II. The PNNL documents include PNL-MA-70 (Part 2), PNL-ALO-212, PNL-ALO-226, and MCS-046. 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 method detection limit (MDL) required to resolve the analyte at one-tenth of the recommended exposure limit for each of the target analytes is achieved using current procedures and with a vapor-sample volume of 3 L and a desorption-solution volume of 3 mL (10 mL for NH_3).

The accuracy of concentration measurements depends on potential errors associated with both sampling and analysis (see Section A.4). Sampling information, including sample volumes, was provided by WHC; sample volume uncertainty was not provided. The uncertainty of analytical results, which depends on the method used, was estimated to be within allowable tolerances (Osborne et al. 1995; Table A.1). For NH_3 analyses, the accuracy of laboratory measurements by selective ion electrode was estimated to be $\pm$ 5% relative, independent of concentration at 1 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-traceable standard reference material (SRM) by using an independent calibration verification standard certified to be NIST traceable. Nitrite analyses (for NO_2 and NO) are performed using certified but not NIST-traceable SRM; this is because NIST does not make a nitrite SRM. Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for NH_3 above, the estimated maximum bias for samples derived from sampling for NO_2 is $\pm$ 10%, and for samples derived from sampling for NO, it is $\pm$ 5% relative. The accuracy of measurements of sample mass is typically $\pm$ 0.1 mg, or much less than 1% of the

Table A.1 Analytical Procedures, Detection Limits, and Expected and Notification Levels for Selected Inorganic Analytes[a]

Analyte	Formula	Procedure	MDL[b] (μg)	MDL[b] (ppmv)	Expected Range[c] (ppmv)	Notification Level[c] (ppmv)
Ammonia	NH_3	PNL-ALO-226	0.1	0.5	≥ 2	≥ 150
Nitrogen Dioxide	NO_2	PNL-ALO-212	0.02	0.02	≥ 0.1	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.02	0.02	≥ 2	≥ 50
Mass (water)[d]	n/a	PNL-TVP-09	0.6 mg	0.2 mg/L	≥ 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) MDL is defined as the vapor concentration that can be detected with an uncertainty equal to about the magnitude of the measurement. The uncertainty is expected to reduce to about one-quarter of the magnitude of the measurement at a concentration of 4 times the MDL. The MDLs were based on the assumption that 3 L of vapor are sampled; if greater volumes of vapor are sampled, correspondingly smaller MDLs may be obtainable. Determination of the MDLs was also based on desorbing-solution volumes of 10 mL for NH_3 and 3 mL for NO and NO_2. The MDL for water was based on the typical variation in the mass change of 5-trap field-blank sorbent trains that accompany samples to the field.

(c) As per Table 7-1 in Osborne et al. (1994). 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.

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 5-trap sorbent train.

A.4 Inorganic Sample Results

Samples were obtained by WHC from the tank headspace of Tank SX-101 on July 21, 1995 using the VSS. The sample job designation number was S5045. Unexposed samples were prepared by PNNL, 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 chain-of-custody (COC) 008912 (Appendix F). The inorganic samples were received from WHC on July 28, 1995; the sample volume information was also received on July 28. Analyses were completed on August 3, 1995 (gravimetric, 13-day hold time), August 11, 1995 (ammonia, 21-day hold time), and August 11, 1995 (nitrite, 21-day hold time).

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table A.2. The types of sample trains used and the order of sorbent traps within each train are also shown in the table. For example, the sorbent train $NH_3/NO_x/H_2O$ contained an NH_3 trap at the inlet end, an NO_x series in the middle (Section A.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table A.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank-headspace concentration results (Table A.3) are

based on this information, and the listed uncertainties equal plus or minus 1 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 were nearly indistinguishable from those of blanks, indicating very low vapor concentrations of the analyte, the concentration results (Table A.3) are listed as "less-than-or-equal-to" a probable maximum value determined by subtracting the average of the blanks less 1 standard deviation from the average of the samples plus 1 standard deviation. 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 3.8 $\pm$ 0.4 part per million by volume (ppmv), based on all 6 samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 0.44 to 0.56 μmol in front sections; NH_3 was not found ($\leq$ 0.01 μmol) in back sorbent sections. Blank corrections, $\leq$ 0.09 μmol in front and $\leq$ 0.05 μmol in back sections, were about 15% of collected quantities. The analysis of 1 sample was duplicated and yielded a repeatability of $\pm$ 0%. One sample leachate was spiked after initial analysis with roughly the quantity of NH_3 in the sample and yielded a percentage recovery of 98%. The continuing calibration verification (CCV) standard, using NIST-traceable material, yielded percentage recoveries of 99, 102, and 104% during the analytical session. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 μg/mL. Although spiked blanks were not tested, the percentage recoveries of 3 sets of blanks spiked with 12.2, 22.3, and 46.4 μmol NH_3 were 101 $\pm$ 4, 109 $\pm$ 2, and 104 $\pm$ 1%, respectively, during previous sample jobs (Clauss et al. 1994; Ligotke et al. 1994).

A.4.2 Nitrogen Oxides Results. It is not known whether the presence of an upstream NH_3 trap typically affects downstream measurements of NO_2 and NO. Consequently, measurements of NO_2 and NO were made using 4 "protected" 5-segment $NH_3/NO_x/H_2O$ and 2 "unprotected" 4-segment NO_x/H_2O sorbent-trap trains. (The NO_x trains consisted of 3 segments: NO_2 trap, oxidizer, NO_2 trap.) A comparison of blank-corrected results from the 2 sampling methods may be made for this sample job (Table A.3): 1) a comparison of NO_2 results indicated a potentially 1.50-fold greater result from the unprotected traps, however, this was not clear because of relatively low measured concentrations; and 2) the unprotected NO concentration results were approximately 0.9-fold less than results from the protected samples, however, the difference was within the variability of the results. Because of the potential uncertainty in these results, measurements using the 2 types of sorbent trap trains are planned to continue during subsequent sample jobs for which NO_x measurements are required and will be evaluated at a later date should significant concentrations (Table A.1) be found in samples from a tank vapor space. No further evaluation is required of the results from this sample job.

The concentrations of NO_2 and NO were 0.10 $\pm$ 0.02 and 0.13 $\pm$ 0.01 ppmv, respectively, based on all 6 samples. Blank-corrected NO_2^- quantities in the sorbent traps averaged 0.0068 μmol (NO_2 samples) and 0.0084 μmol (NO samples). Nitrite blank levels used to correct data were 0.0065 $\pm$ 0.0006 μmol in front (3 of 6 blanks analyzed) and 0.0026 $\pm$ 0.0006 μmol in back (2 of 6 blanks analyzed) sorbent sections. The analyses of 4 samples were duplicated and all yielded repeatabilities of $\pm$ 0% and $\pm$ 1%. Three sample leachates were spiked with 0.25 ppm NO_2^- and yielded percentage recoveries of 104, 96, and 95%. 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

Table A.2 List of PNNL Inorganic Samples, Controls, and Gravimetric Results Obtained from a Heated Tube Inserted into the Headspace of Tank SX-101 on 7/21/95

		Sample Port and Volume Information [a]				
Sample Number	Sorbent Type	Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
Samples:						
S5045-A08-U83	$NH_3/NO_x/H_2O$ Train	5	200.0	15.0	3.00	0.0327
S5045-A09-U84	$NH_3/NO_x/H_2O$ Train	6	200.0	15.0	3.00	0.0328
S5045-A10-U85	NO_x/H_2O Train	7	188.6	15.0	2.83	0.0308
S5045-A11-U86	$NH_3/H_2O/H_2O$ Train	8	193.3	15.0	2.90	0.0318
S5045-A16-U87	$NH_3/NO_x/H_2O$ Train	5	200.0	15.0	3.00	0.0359
S5045-A17-U88	$NH_3/NO_x/H_2O$ Train	6	200.0	15.0	3.00	0.0346
S5045-A18-U89	NO_x/H_2O Train	7	190.3	15.0	2.85	0.0332
S5045-A19-U90	$NH_3/H_2O/H_2O$ Train	8	194.4	15.0	2.92	0.0347
Controls:						
S5045-A25-U91	$NH_3/NO_x/H_2O$ Field Blank	n/a[b]	n/a	n/a	n/a	-0.0013
S5045-A26-U92	$NH_3/NO_x/H_2O$ Field Blank	n/a	n/a	n/a	n/a	-0.0016
S5045-A27-U93	$NH_3/NO_x/H_2O$ Field Blank	n/a	n/a	n/a	n/a	-0.0011

(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.

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 $\pm$ 14, 103 $\pm$ 4, 106 $\pm$ 8, and 111 $\pm$ 7%, respectively (Clauss et al. 1994; Ligotke et al. 1994).

A.4.3 Gravimetric Results. The mass concentration of material collected in the 4- and 5-trap sorbent trains, believed to be primarily water vapor, was 11.8 $\pm$ 0.5 mg/L. The result was based on an average mass gain of 34.6 mg from all 8 ($NH_3/NO_x/H_2O$ and NO_x/H_2O) sample trains. The blank correction applied to the results was + 1.3 mg per train, based on a mass loss of 1.3 $\pm$ 0.3 mg per 3 5-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of $\pm$ 0.1 mg. Although no spiked blanks were tested, the percentage recovery of mass from 3 blank H_2O traps spiked with 51 mg of water was 103 $\pm$ 2% during a previous sample job (Clauss et al. 1994).

Table A.3 Inorganic Vapor Sample Results Obtained from a Heated Tube Inserted into the Headspace of Tank SX-101 on 7/21/95

	Analytical Results (μmol)				
Sample	Front Section	Back Section	Total[a] Blank-Corrected	Sample Volume (L)	Vapor[b] Concentration (ppmv)
NH_3 Samples:			0.50[c]	2.97[c]	3.8 ± 0.4[c]
S5045-A08-U83	0.55	NA[d]	0.46	3.00	3.4
S5045-A09-U84	0.56	0.04	0.47	3.00	3.5
S5045-A11-U86	0.53	NA	0.44	2.90	3.4
S5045-A16-U87	0.65	0.04	0.56	3.00	4.2
S5045-A17-U88	0.65	NA	0.56	3.00	4.2
S5045-A19-U90	0.62	NA	0.53	2.92	4.1
NO_2 Samples:			0.0068	2.95	0.10 ± 0.02
S5045-A08-U83	0.0134	0.0320 x[d]	0.0069	3.00	0.10
S5045-A09-U84	0.0124	0.0059	0.0059	3.00	0.09
S5045-A10-U85[e]	0.0145	0.0062	0.0080	2.83	0.13
S5045-A16-U87	0.0124	0.0072	0.0059	3.00	0.09
S5045-A17-U88	0.0120	NA	0.0055	3.00	0.08
S5045-A18-U89[e]	0.0153	0.0073	0.0088	2.85	0.14
NO Samples:			0.0084	2.95	0.13 ± 0.01
S5045-A08-U83	0.0140	NA	0.0075	3.00	0.11
S5045-A09-U84	0.0150	0.0063	0.0085	3.00	0.13
S5045-A10-U85[e]	0.0143	0.0069	0.0078	2.83	0.12
S5045-A16-U87	0.0167	NA	0.0102	3.00	0.15
S5045-A17-U88	0.0150	0.0063	0.0085	3.00	0.13
S5045-A18-U89[e]	0.0145	0.0061	0.0080	2.85	0.13
Gravimetric Samples:			34.6 mg	2.94	11.8 ± 0.5 mg/L
S5045-A08-U83	n/a	n/a	34.0	3.00	11.3
S5045-A09-U84	n/a	n/a	34.1	3.00	11.4
S5045-A10-U85	n/a	n/a	32.1	2.83	11.3
S5045-A11-U86	n/a	n/a	33.1	2.90	11.4
S5045-A16-U87	n/a	n/a	37.2	3.00	12.4
S5045-A17-U88	n/a	n/a	35.9	3.00	12.0
S5045-A18-U89	n/a	n/a	34.5	2.85	12.1
S5045-A19-U90	n/a	n/a	36.0	2.92	12.3

(a) 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.

(b) 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 nitrate. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks.

(c) Underlined values represent the average of the set samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. Percent RSD may be determined by dividing standard deviation by the average and multiplied by 100. The use of "≤" is defined in Section A.4.

(d) NA = not analyzed; n/a = not applicable; x = not included in determination of average concentration.

(e) NO_x sorbent traps not preceded by an NH_3 trap. Only selected back sorbent sections were analyzed. Results show back sections of ammonia and nitrite samples contain insignificant quantities of the analytes.

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 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 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)[a] Technical Procedure PNL-TVP-02[b]. 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 by PNNL Technical Procedure PNL-TVP-01[c], which is a modification of U.S. Environmental Protection Agency (EPA) compendium Method TO-14. 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. 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[d] 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

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(a) Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

(b) 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.

(c) Pacific Northwest Laboratory. 8/94. *Determination of TO-14 Volatile Organic Compounds in Ambient Air Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-01 (Rev. 0), PNL Technical Procedure, Richland, Washington.

(d) Pacific Northwest Laboratory. 8/94. *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. 0). PNL Technical Procedure, Richland, Washington.

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

Analyte	Formula	Procedure	MDL (ppmv)
Carbon Dioxide	CO_2	PNL-TVP-05	25
Carbon Monoxide	CO	PNL-TVP-05	25
Methane	CH_4	PNL-TVP-05	25
Hydrogen	H_2	PNL-TVP-05	25
Nitrous Oxide	N_2O	PNL-TVP-05	25

the signal sensitivity and lower the detection limit for this analyte. The permanent gases and the derived method detection limit (MDL) are listed in Table B.1.

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 700 part per million by volume (ppmv) using standards at 5 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. A least-squares linear-regression routine was applied to the calibration data set to generate the best line fit for each compound.

Each analyte was quantitated by direct comparison of sample analyte peaks to the calibration plot generated for the compound. The lowest calibration standard for each analyte is reported as the MDL. An MDL for the instrument has not been determined. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within $\pm$ 25% of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N_2 reagent blank, an ambient air sample collected $\sim$10 m upwind of Tank SX-101, and the ambient air collected through the 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 SX-101, ambient air collected $\sim$10 m upwind of the tank, and ambient air collected through the Vapor Sampling System (VSS). The samples were analyzed on July 31, 1995. Carbon dioxide at an average concentration of 338 ppmv was observed in the tank headspace samples. Carbon dioxide in the headspace was at a similar concentration observed in the ambient air. A replicate analysis was performed on SUMMA™ PNL 58; 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 SX-101 and for Ambient Air and Ambient Air Through the VSS Collected Near Tank SX-101 in SUMMA™ Canisters on 7/21/95

Sample	Sample Matrix	PNL Canister Number	Sample Concentration (ppmv)	Average Concentration (ppmv)[a]
CO_2 Samples:				
S5045-A04-057	Tank	057	338	338
S5045-A12-058	Tank	058	335	
S5045-A20-059	Tank	059	340	
S5045-A12-058	Tank[b]	058	338	
S5045-A01-026	Ambient Air - Upwind	026	346	
S5045-A02-031	Ambient Air - VSS	031	347	
CO Samples:				
S5045-A04-057	Tank	057	<25	<25
S5045-A12-058	Tank	058	<25	
S5045-A20-059	Tank	059	<25	
S5045-A12-058	Tank[b]	058	<25	
S5045-A01-026	Ambient Air - Upwind	026	<25	
S5045-A02-031	Ambient Air - VSS	031	<25	
CH_4 Samples:				
S5045-A04-057	Tank	057	<25	<25
S5045-A12-058	Tank	058	<25	
S5045-A20-059	Tank	059	<25	
S5045-A12-058	Tank[b]	058	<25	
S5045-A01-026	Ambient Air - Upwind	026	<25	
S5045-A02-031	Ambient Air - VSS	031	<25	
H_2 Samples:				
S5045-A04-057	Tank	057	<25	<25
S5045-A12-058	Tank	058	<25	
S5045-A20-059	Tank	059	<25	
S5045-A12-058	Tank[b]	058	<25	
S5045-A01-026	Ambient Air - Upwind	026	<25	
S5045-A02-031	Ambient Air - VSS	031	<25	
N_2O Samples:				
S5045-A04-057	Tank	057	<25	<25
S5045-A12-058	Tank	058	<25	
S5045-A20-059	Tank	059	<25	
S5045-A12-058	Tank[b]	058	<25	
S5045-A01-026	Ambient Air - Upwind	026	<25	
S5045-A02-031	Ambient Air - VSS	031	<25	

(a) Average concentrations are reported for the tank matrix and do not include duplicate analysis results or the ambient air results.
(b) Analytical duplicate of tank sample used to determine analytical precision.

Appendix C

Tank Vapor Characterization:

Total Non-Methane Hydrocarbons

Appendix C

Tank Vapor Characterization: Total Non-Methane Hydrocarbons

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)[a] Technical Procedure PNL-TVP-02[b]. 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 by PNNL Technical Procedure PNL-TVP-01[c], which is a modification of U.S. Environmental Protection Agency compendium Method TO-14. 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. 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 Pacific Northwest National Laboratory (PNNL)[d] Technical Procedure PNL-TVP-08[e], 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 nonmethanic organic compounds (TNMOC) concentration in the tank samples.

The method uses an EnTech 7000 cryoconcentration system interfaced with a Hewlett Packard 5890 gas chromatograph/flame ionization detector (GC/FID). The EnTech concentrator is used to pull a metered volume of 50 to 100 mL of sample air from the SUMMA™ canister mounted on an EnTech 7016CA 16-canister autosampler. The sample is cryogenically concentrated, and constituents

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(a) Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

(b) 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.

(c) Pacific Northwest Laboratory. 8/94. *Determination of TO-14 Volatile Organic Compounds in Ambient Air Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-01 (Rev. 0), PNL Technical Procedure, Richland, Washington.

(d) Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

(e) Pacific Northwest Laboratory. 6/95. *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. 0), PNL Technical Procedure, Richland, Washington.

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.

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 PAP-70-1201, Calibration Control.

The TNMOC is calibrated by using propane as the calibration standard and using that response factor as an external standard method. The instrument calibration mixture for the PNL-TVP-08 analysis consists of National Institute for Standards and Technology (NIST) 99.999% propane analyzed using a 5-point, multilevel, linear regression curve.

A NIST 3-part per million by volume (ppmv) propane standard is analyzed as a calibration check with the appropriate blanks and samples run subsequently. The initial calibration is 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, 2 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 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 5-point multilevel calibration curve from the propane standard using the following equation:

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

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

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

C.4 Total Non-Methane Hydrocarbons Sample Results

Table C.2 lists results of the TO-12 gas analysis from samples collected from the headspace of SX-101, ambient air collected ~10 m upwind of the tank, and ambient air collected through the Vapor Sampling System (VSS). The samples were analyzed on August 9, 1995. Concentrations in the ambient air samples ranged from 0.52 mg/m^3 to 0.56 mg/m^3. Concentrations in the 3 tank headspace samples ranged from 0.84 mg/m^3 to 1.24 mg/m^3 with an average concentration of 0.98 mg/m^3. This compares to 0.38 mg/m^3 for the sum of all compounds identified in the target and tentatively identified compound analysis of the SUMMA™ canisters. A replicate analysis was performed on SUMMA™ PNL 58; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

Table C.1. TO-12 Results for Samples Collected from the Headspace of Tank SX-101 and for Ambient Air and Ambient Air Through the VSS Collected near Tank SX-101 in SUMMA ™ Canisters on 7/21/95

	Ambient Air Upwind S5-045-A01.026[a] PNL 026[b] Concentration (mg/m^3)	Ambient Air Through VSS S5-045-A02.031[a] PNL 031[b] Concentration (mg/m^3)	Tank Samples				Average Concentration Tank Samples (mg/m^3)
			S5-045-A04.057[a] PNL 057[b] Concentration (mg/m^3)	S5-045-A12.058[a] PNL 058[b] Concentration (mg/m^3)	S5-045-A20.059[a] PNL 059 [b] Concentration (mg/m^3)	S5-045-A12.058[a] PNL 058 [b][c] Concentration (mg/m^3)	
TO-12	0.56	0.52	0.84	1.24	0.88	1.58	0.98

(a) WHC sample identification number.
(b) PNL canister number.
(c) Replicate analysis for PNL 058; results are not included in the calculation of average concentrations.

Appendix D

Tank Vapor Characterization:

Volatile Organic Analytes

Appendix D

Tank Vapor Characterization: Volatile Organic Analytes

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 National Laboratory (PNNL)[a] Technical Procedure PNL-TVP-02[b]. 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 by PNNL Technical Procedure PNL-TVP-01[c], which is a modification of the U.S. Environmental Protection Agency (EPA) compendium Method TO-14. 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[d], which is a modified version of EPA compendium Method TO-14. The method uses EnTech 7000 cryoconcentration systems interfaced with a 5972 Hewlett Packard (HP) benchtop gas chromatography/ mass spectrometry (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 minutes, and ramp at 4°C per minute to a final temperature of 260°C, with a 5-minute hold. Twenty-four hours before the analysis, the SUMMA™ canister samples were pressurized with purified

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(b) 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.

(c) Pacific Northwest Laboratory. 8/94. *Determination of TO-14 Volatile Organic Compounds in Ambient Air Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-01 (Rev. 0). PNL Technical Procedure, Richland, Washington.

(d) Pacific Northwest Laboratory. 8/94. *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. 0), PNL Technical Procedure, Richland, Washington.

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.

The instrument calibration mixture consists of 51 organic analytes. These 51 compounds that are directly quantified in this analysis make up the target analyte list (these 51 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 calibration mixture with a mixture created using a Kin-Tek® permeation-tube standard 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 4 aliquot sizes ranging from 30 mL to 200 mL, and

Table D.1 Target Organic Analytes

Dichlorodifluoromethane	p-Xylene
Chloromethane	m-Xylene
1,2-Dichloro-1,1,2,2-tetrafluoroethane	Styrene
Vinyl Chloride	1,1,2,2-Tetrachloroethane
Bromomethane	o-Xylene
Chloroethane	1,3,5-Trimethylbenzene
Trichlorofluoromethane	1,2,4-Trimethylbenzene
1,1-Dichloroethene	1,3-Dichlorobenzene
Methylene Chloride	1,4-Dichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichlorobenzene
1,1-Dichloroethane	1,2,4-Trichlorobenzene
cis-1,2-Dichloroethene	Hexachloro-1,3-butadiene
Chloroform	2-Butanone
1,2-Dichloroethane	Acetone
1,1,1-Trichloroethane	Acetonitrile
Benzene	Heptane
Carbon Tetrachloride	Tetrahydrofuran
1,2-Dichloropropane	Pyridine
Trichloroethene	Butanenitrile
cis-1,3-Dichloropropene	Cyclohexane
trans-1,3-Dichloropropene	Decane
1,1,2-Trichloroethane	Ethylbenzene
Toluene	Propanol
1,2-Dibromoethane	Propanenitrile
Tetrachloroethylene	Cyclohexanone
Chlorobenzene	

(a) Pacific Northwest Laboratory. 8/94. *Preparation of TO-14 Volatile Organic Compounds Gas Standards,* PNL-TVP-06 (Rev. 0). PNL Technical Procedure, Richland, Washington.

a response factor for each compound was calculated. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. Performance-based detection limits for the target analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 ppbv is used.

D.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "high-sensitivity tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated using a standard gas mixture containing 39 volatile organic compounds listed in EPA compendium Method TO-14 and an additional 14 tank-related compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d_5, and bromofluorobenzene was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank headspace samples are analyzed.

D.3.1 Quantitation Results of Target Analytes. The quantitative-analysis results for the target analytes were calculated using the average response factors generated using the IS method described above and in PNL-TVP-03. The conversion from ppbv to mg/m^3 assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

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

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

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

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.

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

The IS level added to all blank, standard, and sample injections was 104 ppbv for bromochloromethane, 101 ppbv for 1,4-difluorobenzene, 98.5 ppbv for chlorobenzene-d_5, and 104 ppbv for bromofluorobenzene. The IS concentrations were converted from ppbv to mg/m^3 at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, 117.6 for chlorobenzene-d_5, and 175.00 for bromofluorobenzene. All calculated sample concentrations were multiplied by a factor of 2 to account for the dilution step described in Section D.2.

D.4 Volatile Organic Sample Results

Five SUMMA™ canisters were returned to the laboratory on July 27, 1995, under Westinghouse Hanford Company (WHC) chain-of-custody (COC) 008913 (see Appendix F). The samples were analyzed on August 24, 1995.

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 SX-101 and through the VSS near Tank SX-101 are presented in Table D.4. A representative total ion chromatogram showing the identity of major constituents is given in Figure D.1

Table D.2 lists the quantitative results for compounds listed as target analytes and TICs. Three target analytes above the 5-ppbv reporting cutoff and 5 TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. Two target analytes and 2 TICs were identified in 2 or more tank headspace samples. Trichlorofluoromethane, (0.14 mg/m^3) and acetone (0.09 mg/m^3) accounted for 100% of the target analytes and 61% of the total concentration identified by both the target and TIC analyses. The total concentration of the target analytes was found to be 0.23 mg/m^3. The only 2 TICs observed in 2 or more of the tank headspace samples were methyl alcohol (0.09 mg/m^3) and 1 butanol (0.06 mg/m^3). The total concentration of the TICs was found to be 0.15 mg/m^3 or 39% of the total concentration identified by both the target and TIC analyses. The total concentration of all the compounds identified was 0.38 mg/m^3. This compares to a total concentration of 0.98 mg/m^3 identified in the TO-12 analysis of the 3 tank headspace samples.

SUMMA™ canister PNL 58 was analyzed in replicate for target analytes and TICs to determine analytical precision. The relative percent difference (RPD) results are presented in Table D.3. The RPD was calculated for analytes detected above the detection limit and found in both replicates. One of 2 target analytes and 3 of 5 TIC had an RPD 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 Vapor Sampling System. Acetone and pyridine were the 2 target analytes observed in the ambient air samples. One TIC, 3-buten-2-one, was observed in the upwind ambient air sample.

Hexane and 4-methyl-2-pentanone were not included in the initial calibration standard mix used for the analysis of SX-101. Neither of these compounds were found in the samples as TICs.

Pyridine was found in the canister taken from upwind of the tank at approximately the concentration it was found in the preceding blank sample, indicating carry over or system contamination at a trace level.

The relative response factors for acetonitrile, acetone, and trichlorofluoromethane in the first Continuing Calibration Verification (CCV) increased beyond the 30% acceptance criteria for percent difference (% D) relative to the average response factors derived from the initial calibration, implying that the concentration of these compounds in the samples may be under estimated. The relative response factors for acetonitrile, acetone, trichlorofluoromethane, 1,1,1-trichloroethane, and pyridine increased beyond the acceptance criteria for % D in the second CCV. Again, this implies that concentration of these compounds in the samples may be under estimated.

The absolute area of the 4 IS decreased over the analysis set to a level requiring reporting. This was caused by water induced instrument fatigue. The problem is routinely observed with the HP 5972 GC/MS system because of its poor pumping capacitance. The CCV run after the samples indicated that, with the exceptions noted in the paragraph above, the relative response factors of the target compounds found in the sample held at acceptable levels.

Table D.2. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identified Compounds and Estimated Concentrations[b], for Samples from the Headspce in Tank SX-101 in SUMMA™ Canisters collected on 7/21/95.

Target Analytes	CAS No.	Mol Wt	Ret Time	S5045-A04.057[c] PNL 57[e] (mg/m³)	(ppbv)	S5045-A12.058[c][d] PNL 58[d][e] (mg/m³)	(ppbv)	S5045-A20.059[c] PNL 59[e] (mg/m³)	(ppbv)	Mean and Standard Deviations (mg/m³)	St Dev	(ppbv)	St Dev
Acetonitrile	75-05-8	41.1		<0.01	<5	<0.01	<5	0.01	5	(g)	(g)	(g)	(g)
Acetone	67-64-1	58.1		0.07	27	0.10	39	0.09	35	0.09	0.02	33	6.1
Trichlorofluoromethane	75-69-4	137.4		0.13	21	0.14	22	0.16	26	0.14	0.02	23	2.7
Tentatively Identified Compound[f]													
Methyl Alcohol	67-56-1	32	5.2	0.05	34	0.12	83	0.09	64	0.09	0.04	60	24.7
3-Buten-2-one	78-94-4	70	11.9	<0.03	<10	0.15	46	<0.03	<10	(g)	(g)	(g)	(g)
Butanal	123-72-8	72	12.3	<0.03	<10	0.18	55	<0.03	<10	(g)	(g)	(g)	(g)
1-Butanol	71-36-3	74	16.5	0.05	14	0.09	28	0.05	14	0.06	0.03	19	8.1
Cyclotrisiloxane, hexamethyl-	541-05-9	222	25.6	<0.10	<10	0.13	13	<0.10	<10	(g)	(g)	(g)	(g)

(a) TO-14 plus 14 additonal 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) PNL SUMMA™ canister number.
(f) Obtained by mass spectral interpretation and comparison with the EPA/NIST/WILEY Library.
(g) Mean and/or standard deviation are not meaningful for this analyte.

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 SX-101 on 7/21/95

Target Analytes	CAS No.	Mol Wt	Ret Time	S5045-A12.058[c] PNL 58[d] (mg/m^3)	S5045-A12.058[c] PNL 58[d] (ppbv)	S5045-A12.058[c] PNL 58[d] (mg/m^3)	S5045-A12.058[c] PNL 58[d] (ppbv)	Relative Percent Difference %
Acetonitrile	75-05-8	41.1		<0.01	<5	<0.01	< 5	
Acetone	67-64-1	58.1		0.10	39	0.09	35	10.5
Trichlorofluoromethane	75-69-4	137.4		0.14	22	0.14	23	0.0
Tentatively Identified Compound[e]								
Methyl Alcohol	67-56-1	32	5.2	0.12	83	0.04	26	105.1
3-Buten-2-one	78-94-4	70	11.9	0.15	46	0.15	47	2.0
Butanal	123-72-8	72	12.3	0.18	55	0.19	58	5.5
1-Butanol	71-36-3	74	16.5	0.09	28	0.11	32	13.1
Cyclotrisiloxane, hexamethyl-	541-05-9	222	25.6	0.13	13	0.12	12	3.3

(a) TO-14 plus 14 additonal target analytes.
(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
(c) WHC sample identification number.
(d) PNL SUMMA™ canister number.
(e) Obtained by mass spectral interpretation and comparison with the EPA/NIST/WILEY Library.

Table D.4. Positively Identified and Quantitated Target Analytes(a), Tentatively Identified and Estimated Concentrations[b], in AmbientAir and Ambient Air Through the VSS Collected Near Tank SX-101 in SUMMA™ Canisters on 7/21/95

Target Analytes	CAS No.	Mol Wt	Ret Time	Ambient Air Upwind S5045-A01.026[c] PNL 26[d] (mg/m³)	(ppbv)	Ambient Air Through VSS S5045-A02.031[c] PNL 31[d] (mg/m³)	(ppbv)
Acetone	67-64-1	58.08		0.06	22	0.03	11
Pyridine	110-86-1	79.1		0.04	12	<0.03	<5
Tentatively Identified Compound[b].							
3-Buten-2-one	78-94-4	70	11.9	0.08	27	<0.03	<10

(a) TO-14 plus 14 additonal analytes.
(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
(c) WHC sample identification number.
(d) PNL canister number.

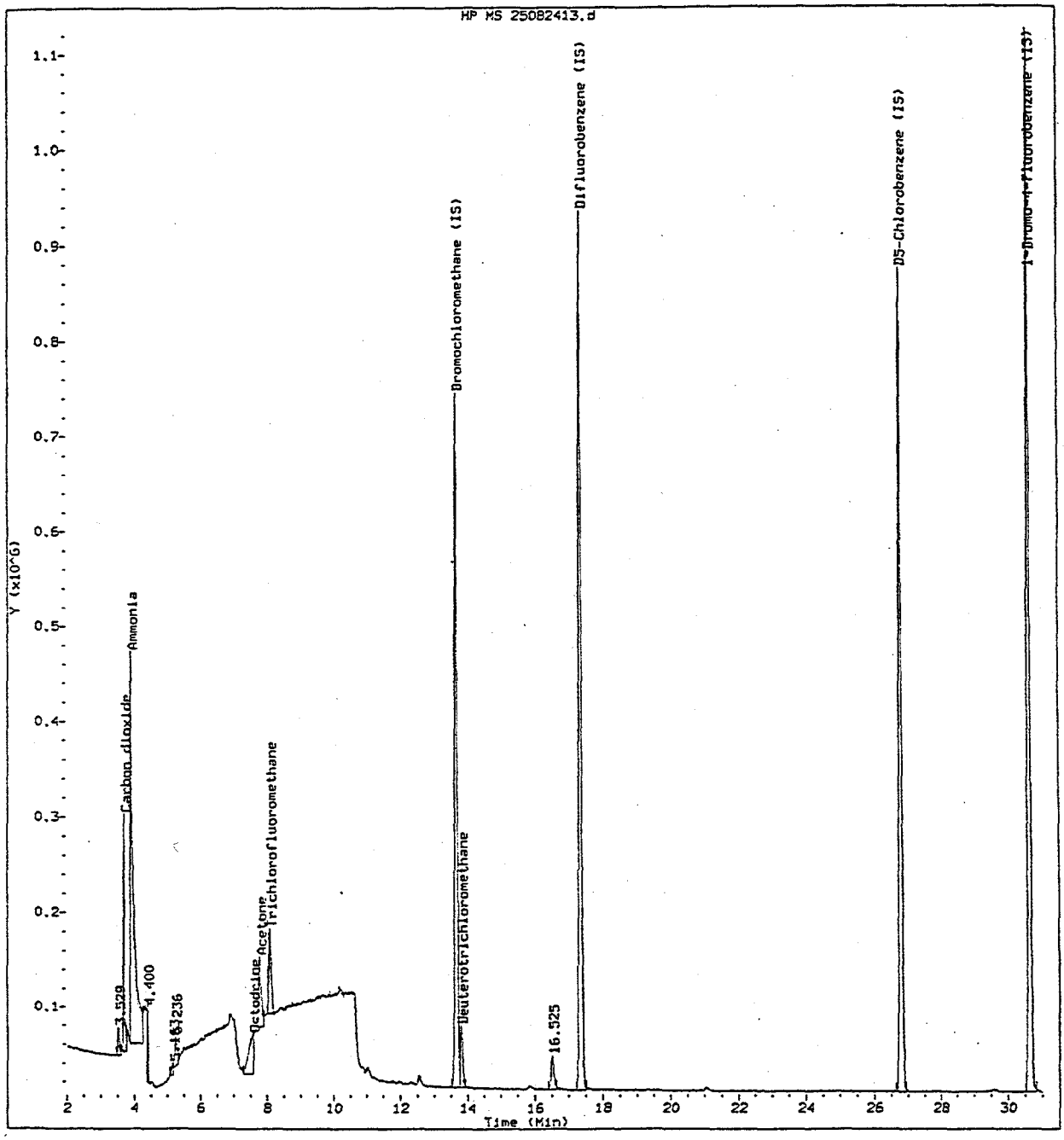

Figure D.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank SX-101 SUMMA™ Canister Sample S5045-A04-057 Collected on 7/21/95

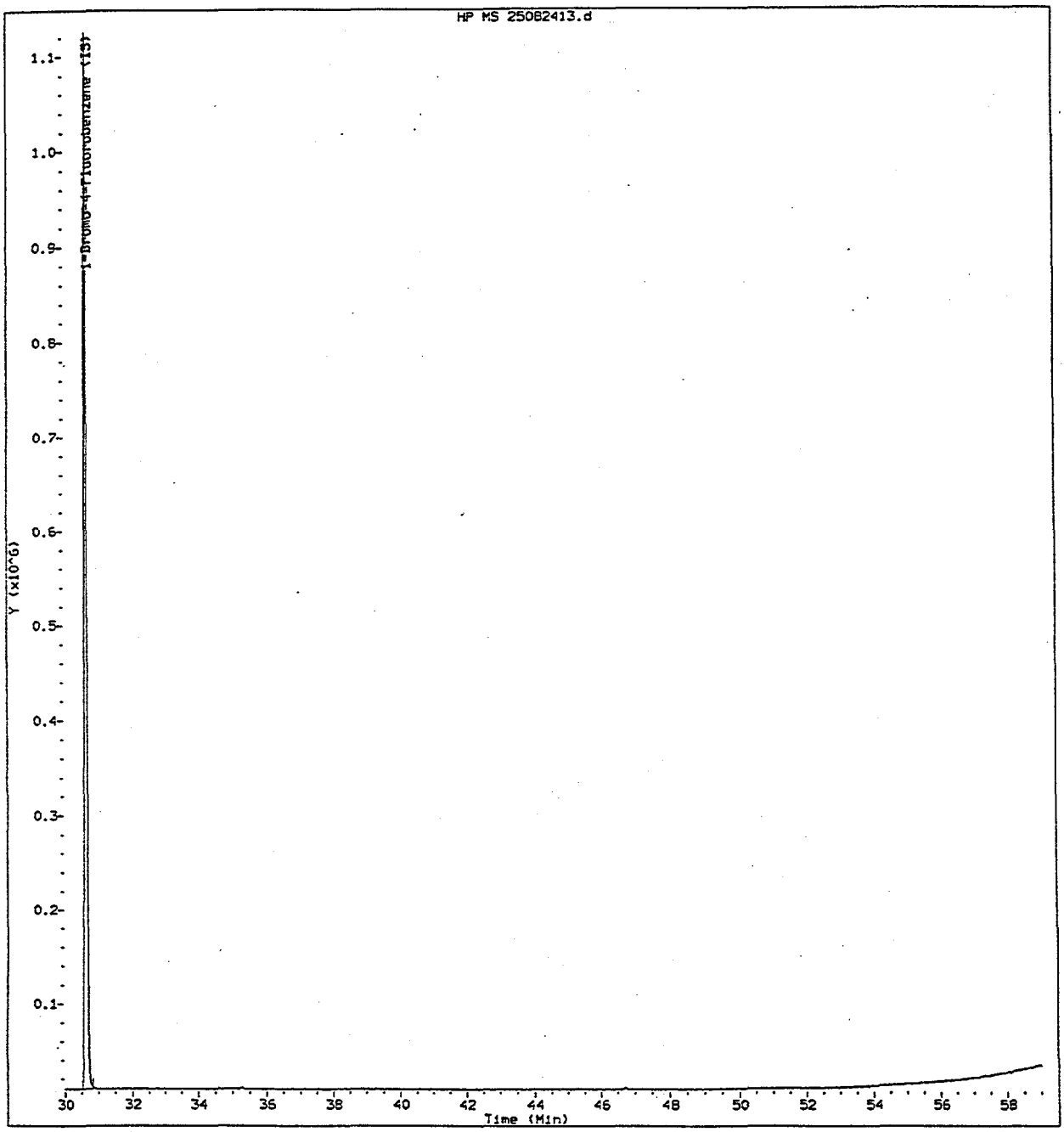

Figure D.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank SX-101 SUMMA™ Canister Sample S5045-A04-057 Collected on 7/21/95

Appendix E

Tank Vapor Characterization:

Semi-Volatile Organic Analytes

Appendix E

Tank Vapor Characterization: Semi-Volatile Organic Analytes

E.1 Sampling Methodology

Samples are collected on Supelco 300 graphite based triple sorbent traps (TSTs). Before field deployment, each trap is heated to 380°C under inert gas flow for a minimum of 60 minutes. 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 individual 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)], which was developed specifically for this activity. 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 1 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 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.

(a) Pacific Northwest Laboratory. 7/95. *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. 0), PNL Technical Procedure, Richland, Washington.

The instrument calibration mixture for the TST analysis consists of 53 organic analytes These 53 compounds that are directly quantified in this analysis make up the target analyte list (these 53 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 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. Performance-based detection limits for the target analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 part per billion by volume (ppbv) is used.

Table E.1 Target Organic Analytes

Dichlorodifluoromethane	m-Xylene
Chloromethane	Styrene
1,2-Dichloro-1,1,2,2-tetrafluoroethane	1,1,2,2-Tetrachloroethane
Vinyl Chloride	o-Xylene
Chloroethane	1,3,5-Trimethylbenzene
Trichlorofluoromethane	1,2,4-Trimethylbenzene
1,1-Dichloroethene	1,3-Dichlorobenzene
Methylene Chloride	1,4-Dichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichlorobenzene
1,1-Dichloroethane	1,2,4-Drichlorobenzene
cis-1,2-Dichloroethene	Hexachloro-1,3-butadiene
Chloroform	2-Butanone
1,2-Dichloroethane	*Acetone*
1,1,1-Trichloroethane	*Acetonitrile*
Benzene	Heptane
Carbon Tetrachloride	Tetrahydrofuran
1,2-Dichloropropane	Pyridine
Trichloroethene	Butanenitrile
cis-1,3-Dichloropropene	Cyclohexane
trans-1,3-Dichloropropene	Decane
1,1,2-Trichloroethane	Hexane
Toluene	4-Methyl-2-pentanone
1,2-Dibromoethane	Propanenitrile
Tetrachloroethylene	Cyclohexanone
Ethylbenzene	Propanol
p-Xylene	Chlorobenzene
1-Butanol	

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.

E.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-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 52 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 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. A continuing calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample.

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

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

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.

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

The IS concentrations were converted from ppbv to mg/m^3 at STP using a molecular weight of 114.09 for 1,4-difluorobenzene, 117.6 for chlorobenzene-d_5, and 174.0 for 1,4 bromofluorbenzene.

E.4 Semi-Volatile Organic Sample Results

Ten TSTs consisting of 6 samples, 2 field blanks, and 2 trip blanks were returned to the laboratory on July 27, 1995, under WHC chain-of-custody 008914. The samples were analyzed September 18, 1995.

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. Four target analytes above the 5-ppbv reporting cutoff and 3 TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. Two of 4 target analytes and none of the TICs were observed in 2 or more sorbent traps. Trichlorofluoromethane, (0.15 mg/m^3) and acetone (0.09 mg/m^3) accounted for 100% of the target analytes and TICs identified by both the analyses. The total concentration of the target analytes was found to be 0.24 mg/m^3.

TST sample PNL 538 was analyzed in replicate for target analytes and TICs to determine analytical precision. The relative percent difference (RPD) results are presented in Table E.3. The RPD was calculated for analytes detected above the detection limit and found in both replicates. None of the 3 target analytes or the single TIC had RPDs of less than 10%.

This tank had very low organic content. The first sample had a very large tributyl phosphate peak with a companion dibutyl butanephosphonate peak. These peaks were completely absent in the other samples. This pattern has been observed in all of the previous samples taken after the cessation of ORNL sampling and appears to be associated with the first sampling port previously used by ORNL. The peak is also associated with elevated 1-butanol which was also the case in previous samples. It is likely that this is a sampling artifact associated with the VSS truck. In future that port should not be used. Continuing Calibration Verification (CCV) samples were generally satisfactory with the exception of tetradecane which showed some spread. The blanks were all clean. Internal standard checks were somewhat more variable than is typical but within acceptable limits. The surrogates showed elevated recoveries in all samples apparently associated with problems with the surrogate standard which was lower than any of the blanks or samples. The samples themselves showed surrogate amounts in the typical range with good precision. Trichlorofluoromethane showed unacceptably large deviations (greater than 35%) from the initial continuing calibration to the second continuing calibration checks. Trichlorofluoromethane was found in all tank samples.

Specific exceptions included:

1. The third CCV with surrogate standard was lost in preparation due to media blowout.

2. The run was interrupted after the start of the third sample in order to allow the HP service engineer install a minor software fix. An update of the instrument name was also done at the same time to provide better Quality Assurance tracking. The autotune file was disrupted as a result of the latter action. Following startup of the first field blank (sample 4) the problem was detected and the run terminated. The correct autotune parameters were restored from the logged daily report, the system baked at 260°C, and the field blank rerun from the split sample. The run proceeded normally from that point with no problems detected.

Since Method PNL-TVP-10 was developed as a new analytical procedure before extensive implementation, some procedural deviations have occurred as noted below.

1. The standard calibration mix was analyzed using four aliquot sizes ranging from 100 mL to 1200 mL. This varied from the procedure, as a 30 mL aliquot size was not analyzed.

2. The surrogates were added to each sample tube before going to the field and they were analyzed in conjunction with each sample with the exception of the system blanks.

3. Procedure PNL-TVP-10 states that four internal standards are used for quantification. One of those standards, bromochloromethane, was removed from the methods before analysis of the tank samples. Bromochloromethane has been found to exhibit unacceptably erratic behavior as an internal standard for the TST method. The next revision of the procedure will reflect this change.

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 SX-101 on 7/21/95.

Target Analytes	CAS No.	Mol Wt	Ret Time	S5045-A05.537[c] PNL 537[e] (mg/m^3)	(ppbv)	S5045-A06.538[c][d] PNL 538[d][e] (mg/m^3)	(ppbv)	S5045-A07.539[c] PNL 539[e] (mg/m^3)	(ppbv)	Mean and Standard Deviations (mg/m^3)	St Dev	(ppbv)	St Dev
Dichlorodifluoromethane	75-71-8	120.9		<0.03	< 5	0.11	20	<0.03	< 5	(g)	(g)	(g)	(g)
Acetone	67-64-1	58.1		0.09	33	0.08	31	0.10	37	0.09	0.01	34	3.3
Trichlorofluoromethane	75-69-4	137.4		0.10	16	0.24	39	0.10	16	0.15	0.08	24	13.4
1-Butanol	71-36-3	74		0.04	12	<0.02	<5	<0.02	<5	(g)	(g)	(g)	(g)
Tentatively Identified Compound[f]													
Ethanol	64-17-5	46	8.5	<0.02	<10	0.03	16	<0.02	<10	(g)	(g)	(g)	(g)
Dibutyl butanephosphonate	78-46-6	250	58.5	0.38	34	<0.11	<10	<0.11	<10	(g)	(g)	(g)	(g)
Phosphoric acid tributyl ester	126-73-8	266	59.2	2.40	202	<0.12	<10	<0.12	<10	(g)	(g)	(g)	(g)

(a) TO-14 plus 14 additonal target analytes.
(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
(c) WHC sample identification number.
(d) Replicate of this sample is found in Table E.3.
(e) PNL sample number.
(f) Obtained by mass spectral interpretation and comparison with the EPA/NIST/WILEY Library.
(g) Mean and/or standard deviation are not meaningful for this analyte.

Table E.3. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identified Compounds and Estimated Concentrations[b] Results of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank SX-101 on 7/21/95

Target Analytes	CAS No.	Mol Wt	Ret Time	S5045-A06.538[c] PNL 538[d] (mg/m^3)	S5045-A06.538[c] PNL 538[d] (ppbv)	S5045-A06.538[c] PNL 538[d] (mg/m^3)	S5045-A06.538[c] PNL 538[d] (ppbv)	Relative Percent Difference %
Dichlorodifluoromethane	75-71-8	120.9		0.11	21	0.09	16	20.0
Acetone	67-64-1	58.1		0.08	31	0.10	37	22.2
Trichlorofluoromethane	75-69-4	137.4		0.24	39	0.20	33	18.2
1-Butanol	71-36-3	74		<0.02	<5	<0.02	<5	
Tentatively Identified Compound[e]								
Ethanol	64-17-5	46	8.5	0.03	16	0.10	49	103.0
Dibutyl butanephosphonate	78-46-6	250	58.5	<0.11	<10	<0.11	<10	
Phosphoric acid tributyl ester	126-73-8	266	59.2	<0.12	<10	<0.12	<10	

(a) TO-14 plus 14 additonal target analytes.
(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
(c) WHC sample identification number.
(d) PNL sample number.
(e) Obtained by mass spectral interpretation and comparison with the EPA/NIST/WILEY Library.

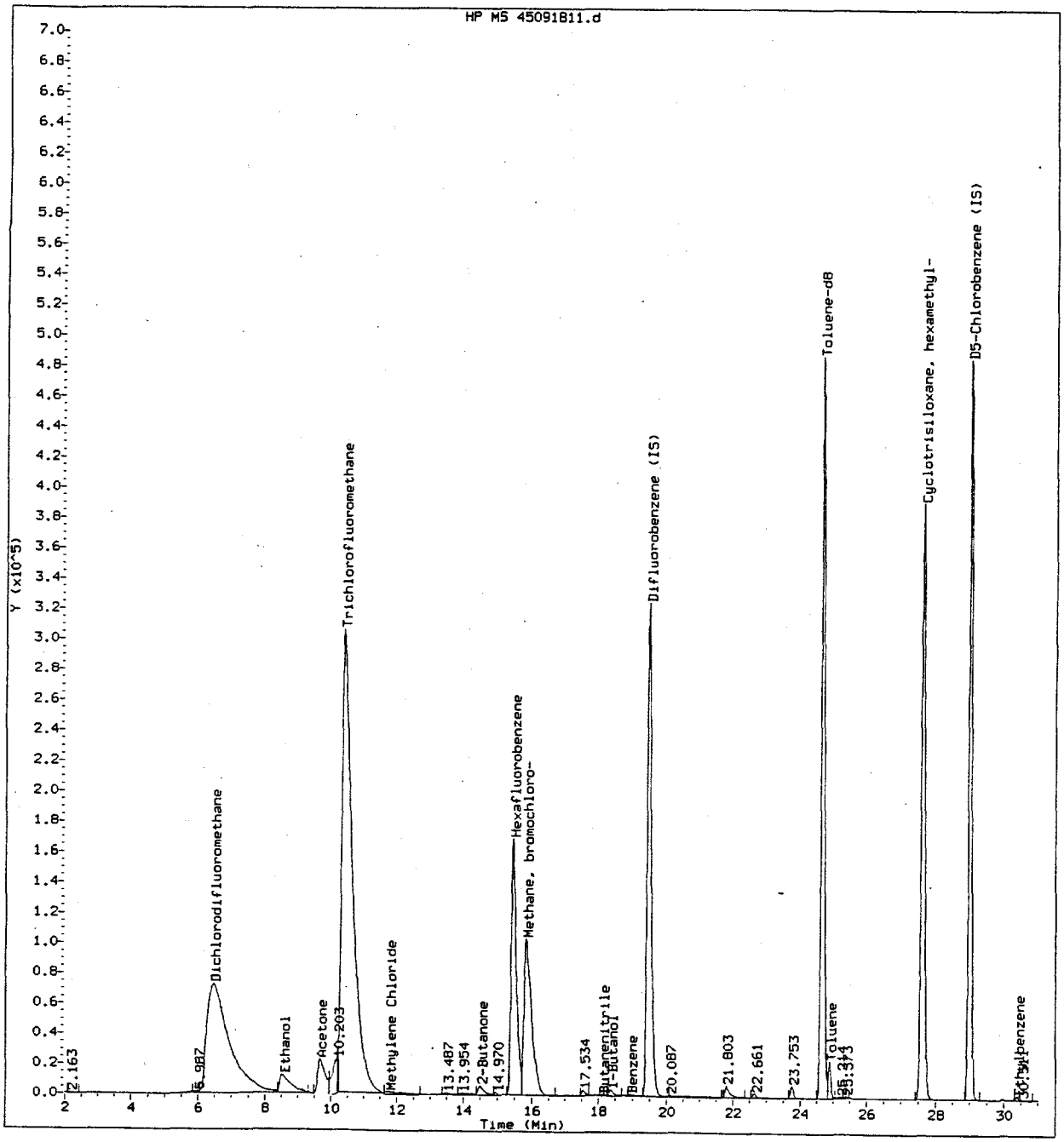

Figure E.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank SX-101 Triple Sorbent Trap Sample S5045-A06-538 Collected on 7/21/95

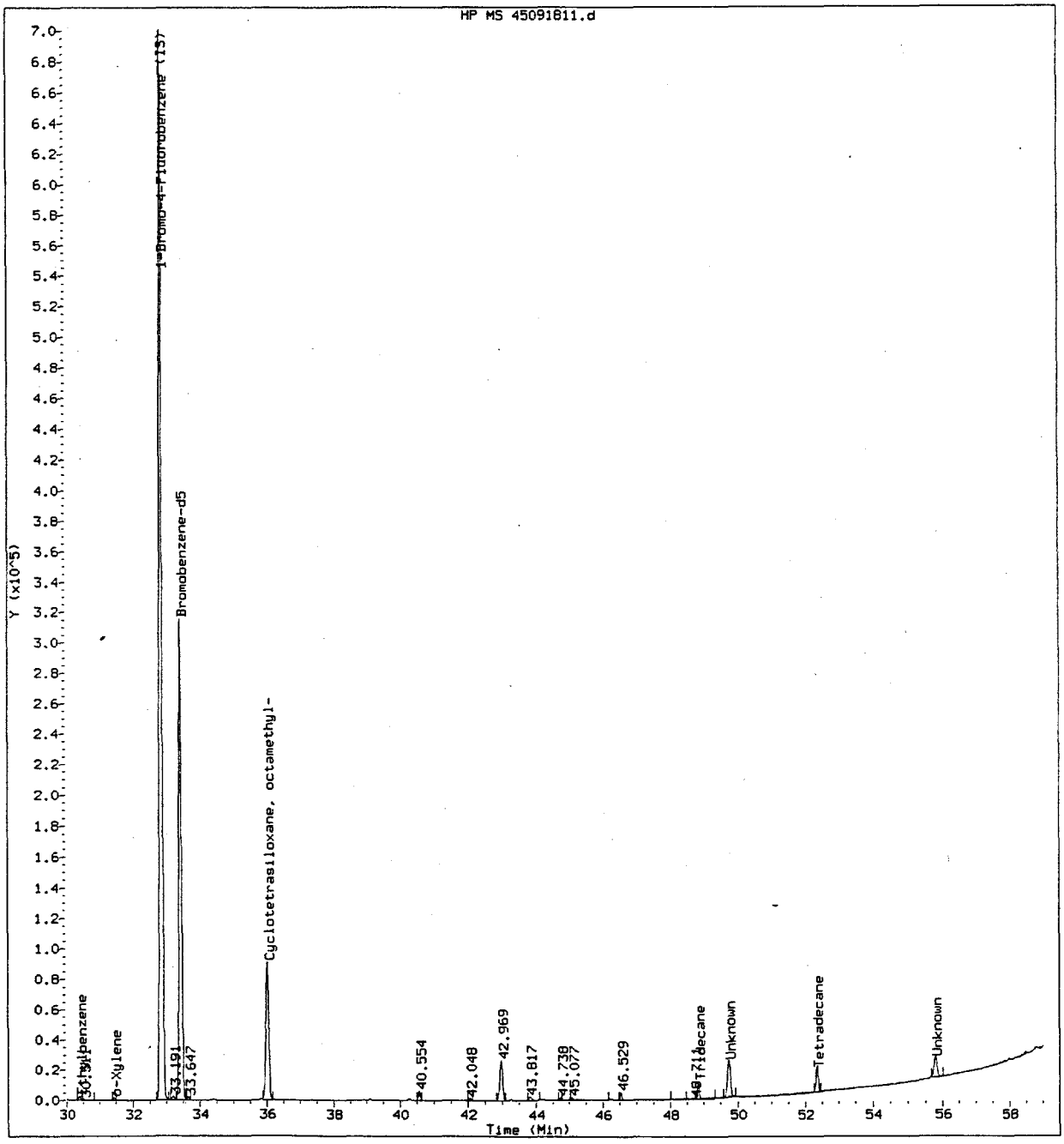

Figure E.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank SX-101 Triple Sorbent Trap Sample S5045-A06-538 Collected on 7/21/95

Appendix F

Tank Vapor Characterization:

Chain of Custody Sample Control Forms

Battelle Pacific Northwest Laboratory	CHAIN OF CUSTODY	WHC 008912

Custody Form Initiator: J. A. Edwards - PNL — 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 West Tank Farm, 241-SX-101 Tank, Vapor Sample SAF S5045 (VSS Truck) — Collection date 07 - 21 - 95; Preparation date 07 - 07 - 95

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: WHC

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

Sample Identification

S5045 - A08 . U83	$NH_3/NO_x/H_2O$	(INORG Sorbent Trap # 1)	Line # 5
S5045 - A09 . U84	$NH_3/NO_x/H_2O$	(INORG Sorbent Trap # 2)	Line # 6
S5045 - A10 . U85	NO_x/H_2O	(INORG Sorbent Trap # 3)	Line # 7
S5045 - A11 . U86	$NH_3/H_2O/H_2O$	(INORG Sorbent Trap # 4)	Line # 8
S5045 - A16 . U87	$NH_3/NO_x/H_2O$	(INORG Sorbent Trap # 5)	Line # 5
S5045 - A17 . U88	$NH_3/NO_x/H_2O$	(INORG Sorbent Trap # 6)	Line # 6
S5045 - A18 . U89	NO_x/H_2O	(INORG Sorbent Trap # 7)	Line # 7
S5045 - A19 . U90	$NH_3/H_2O/H_2O$	(INORG Sorbent Trap # 8)	Line # 8
S5045 - A25 . U91	$NH_3/NO_x/H_2O$	(INORG Field Blank # 1))	
S5045 - A26 . U92	$NH_3/NO_x/H_2O$	(INORG Field Blank # 2)	
S5045 - A27 . U93	$NH_3/NO_x/H_2O$	(INORG Field Blank # 3))	

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

Relinquished By	Date	Time	Received By	Date	Time
G W Dennis	07-10-95	1335	J A Edwards	07-10-95	1335
J A Edwards	07-10-95	1410	T B Utecht	07-10-95	1410
T B Utecht	7-28-95	1315	J A Edwards	07-28-95	1315
J A Edwards	8-3-95	1150	G W Dennis	08-3-95	1150
G W Dennis	8-4-95	0945	K H Pool	8-4-95	0945

Final Sample Disposition

Comments:

	PNL (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	
◊	Sorbents shipped on ice? (<10°C)	(Y) N	/ (Y) N	
◊	Rad release stickers on samples?		/ (Y) N	
◊	Activity report from 222S?		/ (Y) N	
◊	COC copy for LRB, RIDS filed?		/ (Y) N	
◊	COC copy for sorbent follow-on?		/ (Y) N	Original COC follows sorbent media
	POC	(JE)	POC	(JE)

(Revised 05/10/95 PNL)

Battelle Pacific Northwest Lab	CHAIN OF CUSTODY	WHC 008913

Custody Form Initiator: J. A. Edwards - PNL
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 West Tank Farm
241-SX-101 Tank Vapor Sample SAF S5045
(VSS Truck)
Collection date 07 - 27 - 95
Preparation date 07 - 07 - 95

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: PNL

Possible Sample Hazards/Remarks: Unknown at time of sampling

Sample Identification

S5045 - A01 . 026	Ambient Air SUMMA #1 Upwind of SX-101
S5045 - A02 . 031	Ambient Air SUMMA #2 Through Port # 15
S5045 - A04 . 057	SUMMA #3 Port # 15
S5045 - A12 . 058	SUMMA #4 Port # 15
S5045 - A20 . 059	SUMMA #5 Port # 13

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

Relinquished By	Date	Time	Received By	Date	Time
J A Edwards J A Edwards	07-10-95	1410	T B Utecht T. B. Utecht	07-10-95	1410
T.B. Utecht T. B. Utecht	7-27-95	1315	J A Edwards J A Edwards	7-27-95	1315

Final Sample Disposition

Comments:

	PNL (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	
◊	COC copy for LRB, RIDS filed?		/ (Y) N	
		POC (LE)	POC (LE)	

(Revised 10/17/94 PNL)

Battelle Pacific Northwest Laboratory	CHAIN OF CUSTODY	WHC 008914

Custody Form Initiator	J. A. Edwards - PNL	Telephone Page	(509) 373-0141 85-3009 / P8-08 / FAX 376-0418
Company Contact	R. D. Mahon - WHC	Telephone Page	(509) 373-7437 85-9656 / S3-27 / FAX 373-7076
Project Designation/Sampling Locations 241-SX-101 Tank	200 West Tank Farm Vapor Sample SAF S5045 (VSS Truck)	Collection date Preparation date	07- 21- 95 07 - 07 - 95
Ice Chest No.		Field Logbook No. WHC-	N-647-10
Ertco Hi/Lo thermometer No.	PNL-T-006 7/10		
Bill of Lading/Airbill No.	N/A	Offsite Property No.	N/A
Method of Shipment	Government Truck		
Shipped to	WHC		
Possible Sample Hazards/Remarks	Unknown at time of sampling		

Sample Identification

S5045 - A05 . 537	PNL Triple Sorbent Trap (TST) Sample # 1	Line # 1
S5045 - A06 . 538	PNL TST Sample # 2	Line # 2
S5045 - A07 . 539	PNL TST Sample # 3	Line # 3
S5045 - A13 . 540	PNL TST Sample # 4	Line # 1
S5045 - A14 . 541	PNL TST Sample # 5	Line # 2
S5045 - A15 . 542	PNL TST Sample # 6	Line # 3
S5045 - A21 . 543	Open, close & store PNL TST Field Blank # 1	In VSS truck
S5045 - A22 . 544	Open, close & store PNL TST Field Blank # 2	In VSS truck
S5045 - A23 . 545	Store PNL TST Trip Blank # 1	None
S5045 - A24 . 546	Store PNL TST Trip Blank # 2	None

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

Relinquished By	Date	Time	Received By	Date	Time
J A Edwards JA Edwards	07-10-95	1410	T B Utecht TB Utecht	07-10-95	1410
T. B Utecht TB Utecht	7-27-95	1315	JAEdwards JA Edwards	07-27-95	1315

Final Sample Disposition

Comments:

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

Comments:

Cooler Temperature Status

IHi -12 °C / Lo -12 °C (pick up at PNL to WHC)

IHi ___ °C / Lo ___ °C (delivery at WHC from PNL)

IHi ___ °C / Lo ___ °C (at return to PNL from WHC)

IHi 10 °C / Lo -13 °C (at delivery from WHC to PNL)

(Revised 06/21/95 PNL)

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

Lockheed

Larry Pennington	S7-21
Luther Buckley	R2-12

DOE-RL

Carol Babel	S7-54
Jim Thompson	S7-54