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TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank U-204: Results from Samples Collected on 8/8/95

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Summary

This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-U-204 (Tank U-204) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support safety evaluations and tank-farm operations. The results include air concentrations of selected inorganic and organic analytes and grouped compounds from samples obtained by Westinghouse Hanford Company (WHC) and provided for analysis to Pacific Northwest National Laboratory (PNL). Analyses were performed by the Vapor Analytical Laboratory (VAL) at PNL. Analyte concentrations were based on analytical results and, where appropriate, sample volumes provided by WHC. A summary of the results is listed in Table 1. Detailed descriptions of the analytical results appear in the text.

Table 1. Summary Results of Samples to Characterize the Headspace of Tank U-204 on 8/8/95

Category	Sample Medium	Analyte	Vapor[a] Concentration	Units
Inorganic Analytes	Sorbent Traps	NH_3	0.1 ± 0.1	ppmv
		NO_2	≤ 0.02	ppmv
		NO	≤ 0.01	ppmv
		H_2O	15.9 ± 0.1	mg/L
Permanent Gases	SUMMA™ Canister	CO_2	<25	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	0.86	mg/m^3
Volatile Organics (TO-14)	SUMMA™ Canister	Trichlorofluoromethane	6.55	mg/m^3
		Propane	0.11	mg/m^3
		Dichlorofluoromethane	0.10	mg/m^3
Semi-Volatile Organics (PNL-TVP-10)	Sorbent Traps	Trichlorofluoromethane	3.51	mg/m^3
		1-Chloro-1,1-Difluoroethane	0.60	mg/m^3
		Carbon Tetrachloride	0.04	mg/m^3

(a) Vapor concentrations were determined using sample-volume data provided by WHC and are based on averaged data. Result qualifications are described in Chapter 2 and Appendices A through E.

Acknowledgments

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Glossary

% D	% Difference
CAS	Chemical Abstracts Service
CCV	continuing calibration verification
COC	chain-of-custody
C_v	concentration by volume
DIW	deionized water
EPA	U.S. Environmental Protection Agency
GC/FID	gas chromatography/flame ionization detector
GC/MS	gas chromatography/mass spectrometry
GC/TCD	gas chromatography/thermal conductivity detection
IC	ion chromatography
IL	impact level
IS	internal standard
MDL	method detection limit
NIST	National Institute for Standards and Technology
PNL	Pacific Northwest National Laboratory
ppbv	part per billion by volume
ppm	parts per million
ppmv	part per million by volume
QA	quality assurance
RPD	relative percent difference
RSD	relative standard deviation
SAP	sample and analysis plan
SCIC	suppressed-conductivity ion chromatography
SRM	standard reference material
STP	standard temperature and pressure
SUMMA™	stainless steel, passivated interior canister
TEA	triethanolamine
TIC	tentatively identified compound
TNMOC	total 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-U-204 (Tank U-204) at the Hanford Site in Washington State. Pacific Northwest National Laboratory (PNL)[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 PNL 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 S5037. Samples were collected by WHC on August 8, 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 samples 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 August 3, 1995. Exposed samples and controls were returned to PNL on August 14, 1995. Samples and controls were handled, stored, and transported using chain-of-custody (COC) forms to ensure that sample quality was maintained (Appendix F).

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

Tank-headspace samples were analyzed for

- *permanent gases* using gas chromatography/thermal conductivity detection (GC/TCD)
- *total non-methane 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.

(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 U-204 on 8/8/95 (Sample Job S5037) were analyzed in the PNL 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 concentrations (primarily H_2O) were determined. The average and one standard deviation of concentration results from inorganic sorbent sample trains used to sample headspace vapors were 0.1 ± 0.1 ppmv (NH_3), ≤ 0.02 ppmv (NO_2), ≤ 0.01 ppmv (NO), and 15.9 ± 0.1 mg/L (primarily H_2O). The vapor-concentration results were based on six samples for each compound (seven of 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. Twenty-five of 26 samples (96%) were successfully analyzed and used in the averages. One gravimetric sample was lost due to an error in the analysis. Because spare samples were obtained, no action followed the error. Representative field blanks were also analyzed and used to correct data. One of the four average concentration results (for H_2O) exceeded the minimum of the expected ranges (see Table A.1). The precision of results, based on one standard deviation of all samples, was $\leq 1\%$ (within the target level of $\pm 25\%$) for the analyte 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. This uncertainty range was confirmed by evaluating the variability of field blanks (H_2O). With the exception of the single analytical error (above), no other 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, 009247, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent-gas analysis of Tank U-204 can be found in Appendix B of this report. In summary, no permanent gases were observed above the method detection limit (MDL) in the tank-headspace samples, and carbon dioxide in the headspace samples was at a lower concentration than observed in the ambient air.

2.3 Total Non-Methane Hydrocarbons

The complete results of the TO-12 analysis of Tank U-204 can be found in Appendix C of this report. In summary, the average concentration in the three tank-headspace samples was 0.86 mg/m^3. This compares to 7.02 mg/m^3 for the sum of all compounds identified in the target and tentatively identified compound (TIC) analysis of the SUMMA™ canisters. The large difference between the TO-12 and target/TIC analytical results is due to the high concentration of trichlorofluoromethane in the samples. The FID used for the TO-12 analysis is response insensitive to trichlorofluoromethane.

2.4 Volatile Organic Analytes

The complete results of the TO-14 analysis of Tank U-204 can be found in Appendix D of this report. In summary, 3 target analytes above the 5-ppbv reporting cutoff and 3 TICs above the 10-ppbv reporting cutoff were detected in the tank-headspace samples. The total concentration of the target analytes was found to be 6.64 mg/m^3. The total TIC concentration was found to be 0.38 mg/m^3. The total concentration of all the compounds identified was 7.02 mg/m^3. SUMMA™ canister PNL 118 was analyzed in replicate for target analytes and TICs to determine analytical precision. Both of the target analytes and 2 of 3 TICs had relative percent differences (RPDs) of less than 10%. Pyridine was the observed in the ambient-air sample and pyridine and acetone were observed in the ambient air through the VSS sample.

2.5 Semi-Volatile Organic Analytes

The complete results of the sorbent-trap analysis of Tank U-204 can be found in Appendix E of this report. In summary, 7 target analytes above the 5-ppbv reporting cutoff and 3 TICs above the 10-ppbv reporting cutoff were detected in the tank-headspace samples. Five of 7 target analytes and 1 of 3 TICs were observed in two or more sorbent traps. The total concentration of the target analytes was found to be 3.63 mg/m^3. The total concentration of the TICs was found to be 0.60 mg/m^3. The total concentration of all the compounds identified was 4.23 mg/m^3. Triple-sorbent-trap sample PNL 622 was analyzed in replicate for target analytes and TICs to determine analytical precision. Two of 4 target analytes had RPDs of less than 10%. The lone TIC had an RPD greater than 10%.

As the TST procedure was relatively new, some procedural deviations occurred during implementation. A thorough examination of procedural issues has not revealed any significant issues affecting data quality. A complete discussion of procedural deviations is found in Appendix E.

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 that were common to both analyses. Trichlorofluoromethane was higher in the SUMMA™ canisters, and carbon tetrachloride was higher in the TST sample.

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 U-204 on 8/8/95

Target Analytes	CAS No.	S5037[c] TST Results (mg/m³)	St Dev	S5037[c] SUMMA™ Results (mg/m³)	St Dev	Relative Percent Difference %
Acetone	67-64-1	<0.01		0.03	(d)	na
Trichlorofluoromethane	75-69-4	3.51	0.14	6.55	0.46	-60
Carbon Tetrachloride	56-23-5	0.04	0.00	0.06	0.01	12
Dichlorodifluoromethane	75-71-8	0.03	(d)	<0.03		na
Methylene Chloride	75-09-2	0.02	0.01	<0.02		na
Identified Compounds[b]						
Propane	74-98-6	<0.02		0.11	0.05	na
Methane, dichlorofluoro-	75-43-4	<0.05		0.10	0.01	na
Carbon disulfide	75-15-0	<0.03		0.17	0.02	na
Ethane, 1-chloro-1,1-difluoro-	75-68-3	0.60	(d)	<0.04		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.
(d) Standard deviation not available; compound observed in only two SUMMA™ Canister or Triple Sorbent Trap Sample.
na Not applicable

3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank U-204 on August 8, 1995 (Sample Job S5037). 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 as analytical results indicated that 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.* Procedure 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 (PNL) 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[(a)]. Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNL 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 (supplies 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 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 of DIW) was added. Primary sorbent-tube sample materials and back-up (breakthrough) sorbent-trap materials were analyzed separately using identical procedures. Each analytical session was conducted as follows. Working nitrite standards (0, 0.1, 0.25, and 0.5 ppm) were prepared by diluting a stock nitrite standard with desorbing solution. An initial calibration curve was prepared from the instrument response (chromatographic peak height) versus nitrite standard concentration data for the set of working standards. A calibration verification check using 1 of the midrange standards was performed after the analysis of every 6 samples. If the instrument response indicated that sample

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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.

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

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

A.2.3 Mass (Water) Analysis. Sorbent traps used to make each sample train were weighed using a semi-micro mass balance, after labeling and breaking the glass tube ends, without plastic end caps. 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

The samples were analyzed following PNL Impact Level II. The PNL 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.

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. (1995). Notification levels require verbal and written reports to WHC on completion of preliminary analyses.

(d) The vapor-mass concentration, thought to be largely water vapor, is determined gravimetrically.

The accuracy of measurements of sample mass is typically ± 0.1 mg, or much less than 1% of the mass changes of most samples. The analytical accuracy of measurements of the change in mass of sorbent trains, based on the variability in mass change of field-blank sorbent trains, is determined for each sample job and is typically about ± 1 mg per 5-trap sorbent train.

A.4 Inorganic Sample Results

Samples were obtained by WHC from the tank headspace of Tank U-204 on 8/8/95 using the VSS. The sample-job designation number was S5037. Unexposed samples were prepared by PNL, submitted to WHC for the sample job, and then returned to PNL 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) 009247 (Appendix F). The inorganic samples were received from WHC on 8/14/95; the sample-volume information was received on 8/10/95. Analyses were completed on 8/16/95 (gravimetric, 8 day hold time), 8/18/95 (ammonia, 10 day hold time), and 8/23/95 (nitrite, 15 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 one standard deviation of the individual results from each set of samples. Percentage relative standard deviation (RSD) may be determined by dividing the standard deviation by the average result and multiplying by 100. Where analytical results from samples 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 one standard deviation from the average of the samples plus one 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 0.1 ± 0.1 ppmv, based on all six samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 0.01 to 0.03 μmol in front sections and were about 0.0 μmol in back sections. Blank corrections, ≤ 0.09 μmol in front and ≤ 0.05 μmol in back sections, were about 90% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of ± 6%. One sample leachate was spiked after initial analysis with roughly the quantity of NH_3 in the sample and yielded a percentage recovery of 84%. The continuing calibration verification standard, using NIST-traceable material, yielded percentage recoveries of 105, 111, and 107% 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 three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol of NH_3 were 101 ± 4%, 109 ± 2%, and 104 ± 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 four "protected" 5-segment $NH_3/NO_x/H_2O$ and two "unprotected" 4-segment NO_x/H_2O sorbent-trap trains. (The NO_x trains consisted of three segments: NO_2 trap, oxidizer, NO_2 trap.) A comparison of blank-corrected results from the two sampling methods may be made for this sample job (Table A.3): 1) a comparison of NO_2 results was not clear because of low measured concentrations; 2) a comparison of NO results was not clear because of low measured concentrations. Because of the potential uncertainty in these results, measurements using the two types of sorbent trap trains are planned to continue during subsequent sample jobs for which NO_x measurements are required. The measurements will be evaluated at a later date.

The concentrations of NO_2 and NO were ≤ 0.02 and ≤ 0.01 ppmv, respectively, based on all six samples. Blank-corrected NO_2^- quantities in the sorbent traps averaged ≤ 0.0015 μmol (NO_2 samples) and ≤ 0.0006 μmol (NO samples). Nitrite blank levels used to correct data were 0.0045 ± 0.0003 μmol in front (3 of 6 blanks analyzed) and 0.0016 ± 0.0002 μmol in back (2 of 6 blanks analyzed) sorbent sections. The analyses of four samples were duplicated and yielded repeatabilities of ± 1, ± 2, ± 4, and ± 5%. Four sample leachates were spiked with 0.25 ppm NO_2^- and yielded percentage recoveries of 95, 94, 96, and 96%. A 4-point calibration was performed over a concentration range of 0 to 0.5 μg NO_2^- per mL in the desorbing matrix. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 μmol of NO_2^- during previous sample jobs yielded percentage recoveries of 153 ± 14%, 103 ± 4%, 106 ± 8%, and 111 ± 7%, respectively (Clauss et al. 1994; Ligotke et al. 1994).

Table A.2 List of PNL Inorganic Samples, Controls, and Gravimetric Results Obtained from a Heated Tube Inserted into the Headspace of Tank U-204 on 8/8/95

		Sample Port and Volume Information [a]				
Sample Number	Sorbent Type	Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
Samples:						
S5037-A08-55T	$NH_3/NO_x/H_2O$ Train	5	200.0	15.0	3.00	0.0493
S5037-A09-56T	$NH_3/NO_x/H_2O$ Train	6	200.0	15.0	3.00	0.0490
S5037-A10-57T	NO_x/H_2O Train	7	196.4	15.0	2.95	0.0485
S5037-A11-58T	$NH_3/H_2O/H_2O$ Train	8	200.0	15.0	3.00	0.0486
S5037-A16-59T	$NH_3/NO_x/H_2O$ Train	5	200.0	15.0	3.00	0.0486
S5037-A17-60T	$NH_3/NO_x/H_2O$ Train	6	200.0	15.0	3.00	0.0483
S5037-A18-61T	NO_x/H_2O Train	7	196.2	15.0	2.94	N/A[b]
S5037-A19-62T	$NH_3/H_2O/H_2O$ Train	8	200.0	15.0	3.00	0.0491
Controls:						
S5037-A25-63T	$NH_3/NO_x/H_2O$ Field Blank	n/a[b]	n/a	n/a	n/a	0.0012
S5037-A26-64T	$NH_3/NO_x/H_2O$ Field Blank	n/a	n/a	n/a	n/a	0.0012
S5037-A27-65T	$NH_3/NO_x/H_2O$ Field Blank	n/a	n/a	n/a	n/a	0.0014

(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.

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 15.9 ± 0.1 mg/L. The result was based on an average mass gain of 47.5 mg from seven of all eight ($NH_3/NO_x/H_2O$ and NO_x/H_2O) sample trains. One sample was not analyzed because of an error in the analysis. The blank correction applied to the results was - 1.3 mg per train, based on a mass gain of 1.3 ± 0.1 mg per three 5-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of ± 0.1 mg. Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg of water was 103 ± 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 U-204 on 8/8/95

Sample	Analytical Results (μmol) Front Section	Back Section	Total[b] Blank-Corrected	Sample Volume (L)	Vapor[a] Concentration (ppmv)
NH_3 Samples:			0.02[c]	3.00[c]	0.1 ± 0.1[c]
S5037-A08-55T	0.10	0.04	0.01	3.00	0.1
S5037-A09-56T	0.12	NA[d]	0.03	3.00	0.2
S5037-A11-58T	0.10	NA	0.01	3.00	0.1
S5037-A16-59T	0.11	0.04	0.02	3.00	0.2
S5037-A17-60T	0.09	NA	0.01	3.00	0.1
S5037-A19-62T	0.09	NA	0.01	3.00	0.1
NO_2 Samples:			≤ 0.0015	2.98	≤ 0.02
S5037-A08-55T	0.0060	NA	n/a[d]	3.00	n/a
S5037-A09-56T	0.0047	0.0012	n/a	3.00	n/a
S5037-A10-57T[e]	0.0039	0.0020	n/a	2.95	n/a
S5037-A16-59T	0.0044	0.0018	n/a	3.00	n/a
S5037-A17-60T	0.0044	NA	n/a	3.00	n/a
S5037-A18-61T[e]	0.0042	0.0024	n/a	2.94	n/a
NO Samples:			≤ 0.0006	2.98	≤ 0.01
S5037-A08-55T	0.0047	NA	n/a	3.00	n/a
S5037-A09-56T	0.0048	0.0020	n/a	3.00	n/a
S5037-A10-57T[e]	0.0044	0.0026	n/a	2.95	n/a
S5037-A16-59T	0.0043	NA	n/a	3.00	n/a
S5037-A17-60T	0.0045	0.0020	n/a	3.00	n/a
S5037-A18-61T[e]	0.0043	0.0020	n/a	2.94	n/a
Gravimetric Samples:			47.5 mg	2.99	15.9 ± 0.1 mg/L
S5037-A08-55T	n/a	n/a	48.0	3.00	16.0
S5037-A09-56T	n/a	n/a	47.7	3.00	15.9
S5037-A10-57T	n/a	n/a	47.2	2.95	16.0
S5037-A11-58T	n/a	n/a	47.3	3.00	15.8
S5037-A16-59T	n/a	n/a	47.3	3.00	15.8
S5037-A17-60T	n/a	n/a	47.0	3.00	15.7
S5037-A18-61T	n/a	n/a	NA	2.94	NA
S5037-A19-62T	n/a	n/a	47.8	3.00	15.9

(a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (Table A.2). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrate. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks.

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

(c) 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.

(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 (PNL) Technical Procedure PNL-TVP-02[(a)]. The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNL Technical Procedure PNL-TVP-01[(b)], which is a modification of U.S. Environmental Protection Agency compendium Method TO-14. If the canister is verified as clean and 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 PNL Technical Procedure PNL-TVP-05[(c)] with the exceptions listed in the following text and in the Quality Assurance/Quality Control section of this report. This method was developed in-house to analyze permanent gases, defined as hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and nitrous oxide (N_2O), by gas chromatograph/thermal conductivity detection (GC/TCD). Aliquots of sampled air are drawn directly from each canister into a 5-mL gas-tight syringe and injected into a Hewlett-Packard 5890 GC/TCD fitted with a loop injector valve and a column switching valve. An aliquot of 5 mL is used so that the 1.0-mL injection loop is completely purged with sample air, ensuring that no dilution of the sample takes place within the injection loop. One set of GC conditions is used to analyze for CO, CO_2, N_2O, and CH_4 using Helium (He) as the carrier gas. A second GC analysis is performed for H_2 (using nitrogen as the carrier gas) to enhance the signal sensitivity and lower the detection limit for this analyte. The permanent gases and the derived method detection limit (MDL) are listed in Table B.1.

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

(b) 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.

(c) 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

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 parts per million by volume (ppmv) using standards at five different concentrations and He as a carrier gas. A similar procedure was followed for H_2, except the carrier gas was changed to N_2. 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. An MDL for the instrument has not been determined. The lowest calibration standard for each analyte is reported as the MDL. 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 ~10 m upwind of Tank U-204, 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 U-204, ambient air collected ~10 m upwind of the tank, and ambient air collected through the vapor sampling system. The samples were analyzed on August 15, 1994. No permanent gases were observed above the MDL in the tank-headspace samples. Carbon dioxide in the headspace was at a lower concentration than observed in the ambient air. A replicate analysis was performed on SUMMA™ canister PNL 118; 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 U-204 and for Ambient Air and Ambient Air Through the VSS Collected Near Tank U-204 in SUMMA™ Canisters on 8/8/95

Sample	Sample Matrix	PNL Canister Number	Sample Concentration (ppmv)	Average Concentration (ppmv)[a]
CO_2 Samples:				
S5037-A04-115	Tank	115	<25	<25
S5037-A12-118	Tank	118	<25	
S5037-A20-121	Tank	121	<25	
S5037-A12-118	Tank[b]	118	<25	
S5037-A01-014	Ambient Air - Upwind	014	337	
S5037-A02-023	Ambient Air - VSS	023	333	
CO Samples:				
S5037-A04-115	Tank	115	<25	<25
S5037-A12-118	Tank	118	<25	
S5037-A20-121	Tank	121	<25	
S5037-A12-118	Tank[b]	118	<25	
S5037-A01-014	Ambient Air - Upwind	014	<25	
S5037-A02-023	Ambient Air - VSS	023	<25	
CH_4 Samples:				
S5037-A04-115	Tank	115	<25	<25
S5037-A12-118	Tank	118	<25	
S5037-A20-121	Tank	121	<25	
S5037-A12-118	Tank[b]	118	<25	
S5037-A01-014	Ambient Air - Upwind	014	<25	
S5037-A02-023	Ambient Air - VSS	023	<25	
H_2 Samples:				
S5037-A04-115	Tank	115	<25	<25
S5037-A12 118	Tank	118	<25	
S5037-A20-121	Tank	121	<25	
S5037-A12-118	Tank[b]	118	<25	
S5037-A01-014	Ambient Air - Upwind	014	<25	
S5037-A02-023	Ambient Air - VSS	023	<25	
N_2O Samples:				
S5037-A04-115	Tank	115	<25	<25
S5037-A12-118	Tank	118	<25	
S5037-A20-121	Tank	121	<25	
S5037-A12-118	Tank[b]	118	<25	
S5037-A01-014	Ambient Air - Upwind	014	<25	
S5037-A02-023	Ambient Air - VSS	023	<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 (PNL) Technical Procedure PNL-TVP-02[(a)]. The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNL Technical Procedure PNL-TVP-01[(b)], which is a modification of U.S. Environmental Protection Agency compendium Method TO-14. If the canister is verified as clean and 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 PNL Technical Procedure PNL-TVP-08[(c)], 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 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.

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

(b) Pacific Northwest Laboratory. 8/94. *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.

(c) 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.

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 appropriate blanks and samples run subsequently. The limited calibration is used to quantify 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:

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

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

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

C.4 Total Non-Methane Hydrocarbons Sample Results

Table C.2. lists results of the TO-12 gas analysis from samples collected from the headspace of Tank U-204, ambient air collected ~10 m upwind of the tank, and ambient air collected through the vapor sampling system. The samples were analyzed on August 30, 1995. Concentrations in the ambient-air samples ranged from 0.22 mg/m^3 to 0.26 mg/m^3. Concentrations in the three tank-headspace samples ranged from 0.79 mg/m^3 to 0.90 mg/m^3 with an average concentration of 0.86 mg/m^3. This compares to 7.02 mg/m^3 for the sum of all compounds identified in the target and tentatively identified compound (TIC) analysis of the SUMMA™ canisters. The large difference between the TO-12 and target/TIC analytical results is due to the high concentration of trichlorofluoromethane in the samples. The flame ionization detector used for the TO-12 analysis is insensitive to trichlorofluoromethane. A replicate analysis was performed on SUMMA™ canister PNL 118; 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 U-204 and for Ambient Air and Ambient Air Through the VSS Collected near Tank U-204 in SUMMA ™ Canisters on 8/8/95

	Ambient Air Upwind S5-037-A01.014[a] PNL 014[b] Concentration (mg/m^3)	Ambient Air Through VSS S5-037-A02.023[a] PNL 023[b] Concentration (mg/m^3)	Tank Samples				
			S5-037-A04.115[a] PNL 115[b] Concentration (mg/m^3)	S5-037-A12.118[a] PNL 118[b] Concentration (mg/m^3)	S5-037-A20.121[a] PNL 121 [b] Concentration (mg/m^3)	S5-037-A12.118[a] PNL 118 [b][c] Concentration (mg/m^3)	**Average Concentration Tank Samples (mg/m^3)**
TO-12	0.22	0.26	0.90	0.90	0.79	0.92	0.86

(a) WHC sample identification number.
(b) PNL canister number.
(c) Replicate analysis for PNL 118; 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 (PNL) Technical Procedure PNL-TVP-02[(a)]. The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNL Technical Procedure PNL-TVP-01[(b)], 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 PNL Technical Procedure PNL-TVP-03[(c)], which is a modified version of EPA compendium Method TO-14. The method uses EnTech 7000 cryoconcentration systems interfaced with a 5972 Hewlett-Packard benchtop gas 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 min, and ramp at 4°C per min to a final temperature of 260°C, with a 5-min hold. Twenty-four hours before the analysis, the SUMMA™ canister samples were pressurized with purified air (supplied by Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The starting pressure was first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level

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

(b) Pacific Northwest Laboratory. 8/94. *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.

(c) 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.

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 for the PNL-TVP-03 analysis consists of the standard 39 organic analytes with an additional 14 tank-related compounds. Together, 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 D.1. The calibration mixture was prepared by blending a commercially prepared 39-compound TO-14

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-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
Chlorobenzene	Propanol
Ethylbenzene	

calibration mixture with a 14-compound mixture created using a Kin-Tek® permeation-tube standard generation system. The operation of the permeation-tube system follows the method detailed in PNL Technical Procedure PNL-TVP-06[(a)]. The standard calibration mix was analyzed using four aliquot sizes ranging from 30 mL to 200 mL, and a response factor for each compound was calculated. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. 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 IS (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank-headspace samples are analyzed.

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

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

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

(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.

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:

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

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

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

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

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 August 14, 1994, under Westinghouse Hanford Company (WHC) chain-of-custody 009245 (see Appendix F). The samples were analyzed on August 30, 1994.

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 U-204 and through the VSS near Tank U-204 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 4 TICs above the 10-ppbv reporting cutoff were detected in the tank-headspace samples. All the target analytes and 3 TICs were identified in two or more tank-headspace samples. Trichlorofluoromethane (6.55 mg/m^3), carbon tetrachloride (0.06 mg/m^3), and acetone (0.03 mg/m^3) accounted for 100% of the target analytes and 95% of the total concentration identified by both the target and TIC analyses. The total concentration of the target analytes was found to be 6.64 mg/m^3. The only three TICs observed in these samples were carbon disulfide (0.17 mg/m^3), propane (0.11 mg/m^3), and dichlorofluoromethane (0.10 mg/m^3). The total concentration of the TICs identified was 0.38 mg/m^3 or 5% of the total concentration identified by both the target and TIC analyses. The total concentration measured by

both these analyses was 7.02 mg/m^3. This compares to a total concentration of 0.86 mg/m^3 identified in the TO-12 analysis of the three tank-headspace samples. The large difference between the TO-12 and target/TIC analytical results is due to the high concentration of trichlorofluoromethane in the samples. The flame ionization detector used for the TO-12 analysis is insensitive to trichlorofluoromethane.

SUMMA™ canister PNL 118 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 reporting cutoff and found in both replicates. Two target analytes and 2 of 3 TICs had RPDs of less than 10%.

Table D.4 lists the quantitative results for compounds listed as target analytes and tentatively identified compounds (TICs) in ambient air and ambient air through the vapor sampling system (VSS). Pyridine was found in the ambient-air sample and pyridine and acetone were found in the ambient air through the VSS sample. Pyridine was not found in any of the tank-headspace samples. No TICs were observed in the two ambient-air samples.

The absolute area of the four ISs decreased over the analysis set to a level requiring reporting, based on procedure PNL-TVP-03, Rev. 0 requirements. Changes in IS area may indicate that the instrument was not operating correctly. In this case, the changes in IS areas were caused by water-induced instrument fatigue. This problem is routinely observed with the 5792 Hewlett-Packard GC/MS system because of its poor pumping capacity.

To better understand the importance of the IS area changes, the CCV standard run was evaluated after the samples were analyzed. The CCV standard is an absolute evaluation of the instrument performance relative to the initial calibration. With the exceptions noted above, the relative response factors generated from the final CCV standard agreed well with those in the initial calibration, indicating that, although there was a noted change in absolute IS areas, this change did not significantly affect the relative response factors. Thus, the data strongly suggest that the instrument was within calibration specifications when the sample analysis was completed. Therefore, the results are valid.

The following deviation from procedure PNL-TVP-03 was noted. The compound hexane was not analyzed as a target compound in these samples because a proper standard was not available at the time of analysis. For this analysis, hexane was treated as a TIC when present. This provided a somewhat less accurate measure of the actual concentration of hexane because it was quantified using the response factor of the nearest eluting IS rather than the relative response factor generated from authentic standards. The compound will be added back to the target compound list as soon as the standard becomes available.

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 U-204 in SUMMA™ Canisters collected on 8/8/95.

Target Analytes	CAS No.	Mol Wt	Ret Time	S5037-A04.115[c] PNL 115[e] (mg/m³)	(ppbv)	S5037-A12.118[c][d] PNL 118[d][e] (mg/m³)	(ppbv)	S5037-A20.121[c] PNL 121[e] (mg/m³)	(ppbv)	Mean and Standard Deviations (mg/m³)	St Dev	(ppbv)	St Dev
Acetone	67-64-1	58		0.03	13	<0.01	<5	0.02	9	0.03	(g)	11	(g)
Trichlorofluoromethane	75-69-4	137		6.91	1127	6.03	983	6.72	1096	6.55	0.46	1069	76.0
Carbon Tetrachloride	56-23-5	153.8		0.06	9	0.06	9	0.07	10	0.06	0.01	9	0.7
Pyridine	110-86-1	79		<0.02	< 5	<0.02	< 5	<0.02	< 5	(g)	(g)	(g)	(g)
Tentatively Identified Compound[f]													
Propane	74-98-6	44	4.3	0.09	45	0.16	82	0.07	37	0.11	0.05	55	23.9
Methane, dichlorofluoro-	75-43-4	120	6.7	0.11	20	0.10	19	0.10	18	0.10	0.01	19	1.1
Carbon disulfide	75-15-0	76	10.2	0.18	53	0.15	45	0.18	52	0.17	0.02	50	4.5
Unknown C5 Alkene/Cycloalkane		70	11.9	0.16	50	(h)	(h)	(h)	(h)	(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.
(h) No molecular weight available for calculation

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 U-204on 8/8/95

Target Analytes	CAS No.	Mol Wt	Ret Time	S5037-A12.118[c] PNL 118[d] (mg/m³)	S5037-A12.118[c] PNL 118[d] (ppbv)	S5037-A12.118[c] PNL 118[d] (mg/m³)	S5037-A12.118[c] PNL 118[d] (ppbv)	Relative Percent Difference %
Acetone	67-64-1	58		<0.01	<5	0.01	5	
Trichlorofluoromethane	75-69-4	137		6.03	983	6.63	1082	9.5
Carbon Tetrachloride	56-23-5	153.8		0.06	9	0.06	9	0.0
Pyridine	110-86-1	79		<0.02	< 5	<0.02	< 5	
Tentatively Identified Compound[e]								
Propane	74-98-6	44	4.3	0.16	82	0.03	13	146.2
Methane, dichlorofluoro-	75-43-4	120	6.7	0.10	19	0.11	20	5.8
Carbon disulfide	75-15-0	76	10.2	0.15	45	0.16	47	3.8
Unknown C5 Alkene/Cycloalkane		70	11.9	(f)	(f)	(f)	(f)	

(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.
(f) No molecular weight available for calculation.

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 U-204 in SUMMA™ Canisters on 8/8/95

Target Analytes	CAS No.	Mol Wt	Ret Time	Ambient Air Upwind S5037-A01.014[c] PNL 14[d] (mg/m³)	(ppbv)	Ambient Air Through VSS S5037-A02.023[c] PNL 23[d] (mg/m³)	(ppbv)
Acetone	67-64-1	58		<0.02	<5	0.02	6
Pyridine	110-86-1	79.1		0.04	12	0.04	12

Tentatively Identified Compound[b]

No Compounds Found

(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.

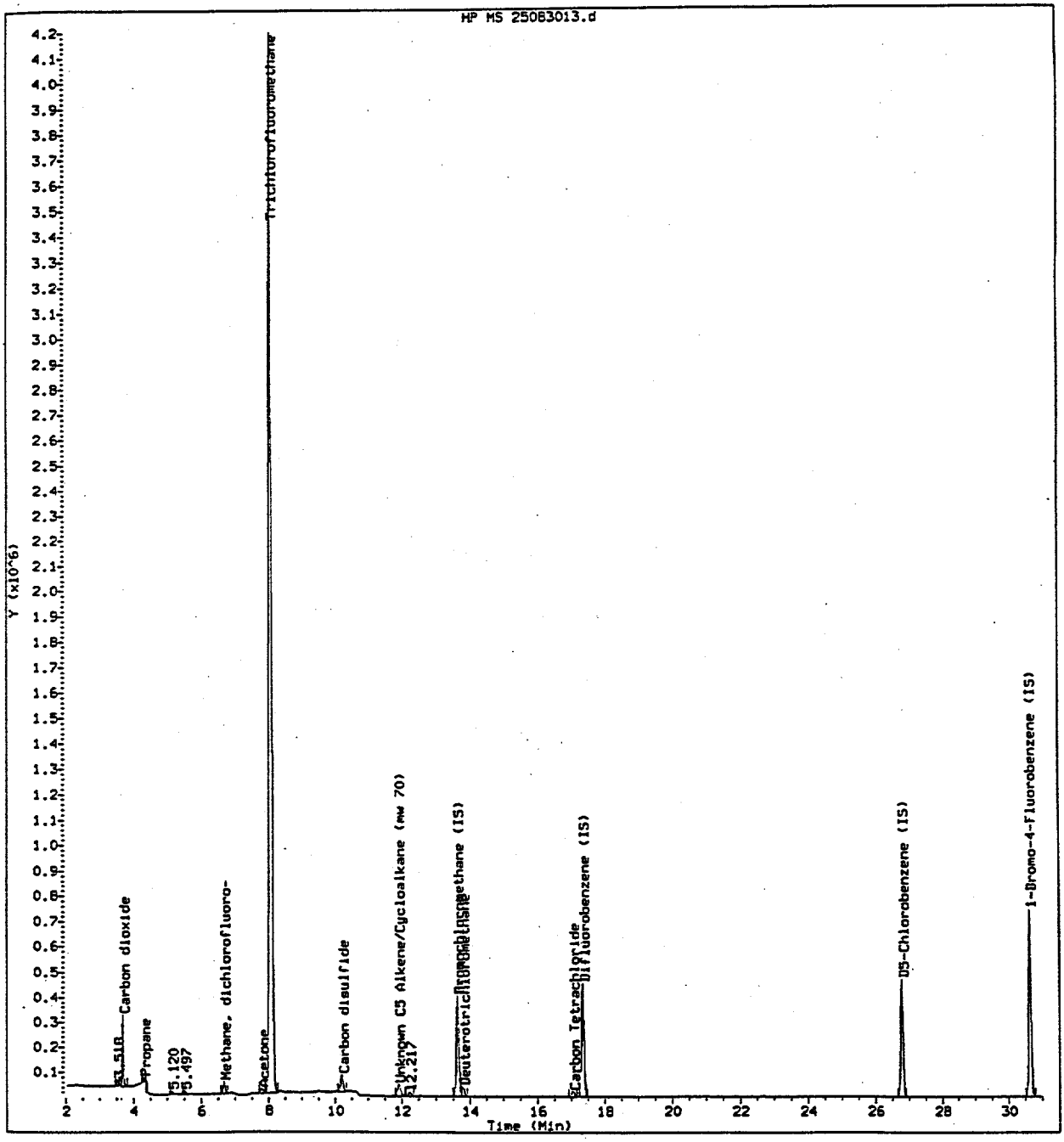

Figure D.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank U-204 SUMMA™ Canister Sample S5037-A04-115 Collected on 8/8/95

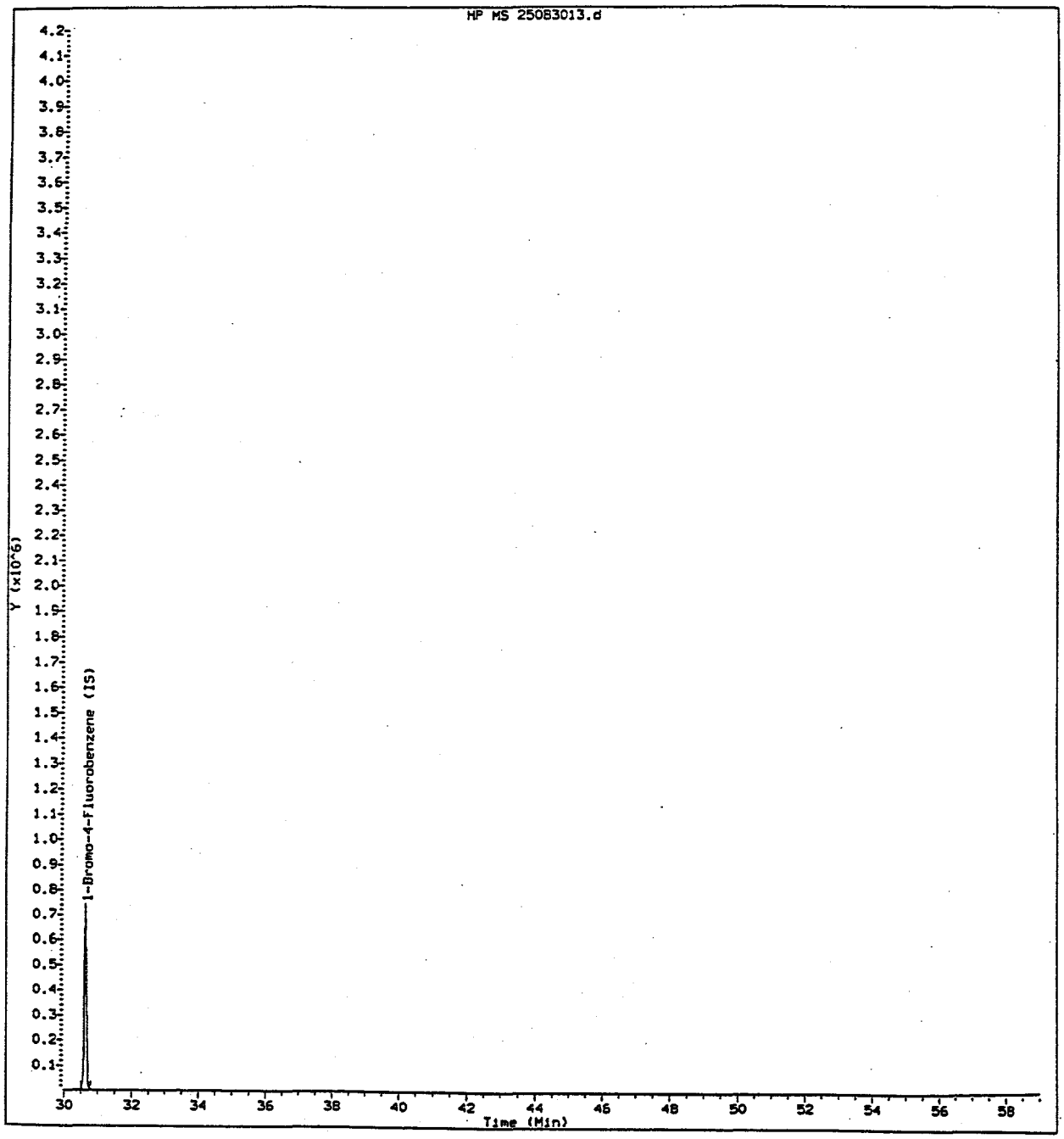

Figure D.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank U-204 SUMMA™ Canister Sample S5037-A04-115 Collected on 8/8/95

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

E.2 Analytical Procedure

The Supelco 300 tubes were analyzed according to Pacific Northwest National Laboratory (PNL) Technical Procedure PNL-TVP-10[(a)], with exceptions noted in Section E.4. The method employs Supelco Carbotrap™ 300 traps for sample collection and preconcentration. The traps are ground-glass tubes (11.5 cm long X 6 mm OD, 4 mm ID) containing a series of sorbents arranged in order of increasing retentivity. Each trap contains 300 mg of Carbotrap™ C, 200 mg of Carbotrap™ B, and 125 mg of Carbosieve™ S-III. The first 2 sorbents are deactivated graphite with limited sorption power for less volatile compounds. The final trapping stage, the Carbosieve™ S-III, is a graphetized molecular sieve used to retain the most volatile components, including some permanent gases such as Freon-12. Following sample collection and addition of IS (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 the standard 37 organic analytes with an additional 14 tank-related compounds. Two compounds typically found on the TO-14 list are not included—bromomethane and benzyl chloride. Together, these 61 compounds that are directly quantified in this analysis make up the target analyte list (these 61 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 parts per billion by volume (ppbv) is used.

Table E.1 Target Organic Analytes

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

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 a full auto tune, as described in PNL-TVP-10. Upon satisfactory completion of the instrument diagnostic check, a blank tube was analyzed to check the cleanliness of the system. The instrument was then calibrated using a 300-mL volume of standard gas mixture containing 61 compounds shown in Table E.1. A gas mixture containing difluorobenzene, chlorobenzene-d_5, and 1,4 bromofluorobenzene was used as an IS for all calibration standard and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. A continuing calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample.

E.3.1 Quantitation Results of Target Analytes. The quantitative-analysis results for the target analytes were calculated directly from the calibration curve generated using the IS method described above and in PNL-TVP-10. It should be noted that the relative response factor value for 1,1,2-trichloroethane was calculated using the second IS, not the first IS, which is nearest in retention time to this compound. The first IS will be used to calculated the relative response factor for this compound for subsequent analyses. The conversion from ppbv to mg/m^3 assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

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. Five target analytes above the 5-ppbv reporting cutoff and 4 TICs above the 10-ppbv reporting cutoff were detected in the tank-headspace samples. Three of 5 target analytes and none of the TICs were observed in 2 or more sorbent traps. Trichlorofluoromethane (0.15 mg/m^3), acetone (0.09 mg/m^3), and butane (0.06 mg/m^3) accounted for 100% of the target analytes and TICs identified by both the target and TIC analyses. The total concentration of the target analytes was found to be 0.30 mg/m^3. No TICs were identified in 2 or more of the tank-headspace samples.

Trichloromethane was detected as a target compound at levels above the upper calibration standard range.

Triple sorbent trap 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 4 target analytes or the single TIC had RPDs of less than 10%.

This run went very smoothly. This was the first run using a new standard with a significantly expanded analyte list. The TO14+ standard now includes 1-butanol and a complete series of n-alkanes ranging from C_4 to C_{14}. A new acetone standard was also added, with acetone returned to the target list. The method has been modified to use the archived surrogate tubes as standards after adding IS and TO14+ standards (300 mL each). Three laboratory blanks containing 300 mL of IS have been added as separators between standards and samples throughout the run as well. This procedure worked very well and will be used in the future. It provides better control of blanks and standards.

The IS checks were fully satisfactory. Blanks were satisfactory. Surrogate recoveries were acceptable for all samples, except for the first field blank, which was slightly low. The last continuing calibration verification (CCV) sample did not have surrogate as the tube was damaged in preparation and was replaced with a clean tube that did not have surrogate in place. The CCV checks

were satisfactory except for tetradecane, which had changed by more than 35%, in the last CCV sample. Tridecane showed some evidence of drift also. It is possible that these two compounds may be of too low a volatility to provide stable calibration by this method.

Specific exceptions included

1. Sample 45091514 had one of the teflon end-cap inserts reversed. This is not expected to have any significant effect.

2. Organic loading was very light on these samples with one exception. The most prominent peak was trichlorofluoromethane, which was present at levels well in excess of the upper calibration range. The other notable feature was the presence of a very large amount of tributyl phosphate (TBP) in the first sample (TBP was completely absent from the other two samples). Some low-level hydrocarbons in the mid-volatility range were present. The pattern was similar to that observed in U-203, but at lower levels. No TICs appeared from that region.

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

1. Two blanks were run at the start of the run sequence, and blanks were added between samples and before the last continuing-calibration sample. However, this run order was not consistent with the procedure. The method will be modified to reflect appropriate placement of blanks throughout the run occurrence.

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

3. Three archived surrogate samples were to be analyzed according to procedure; however, surrogate compounds were added to all samples with the exception of the first field blank and the last continuing calibration sample.

4. Procedure PNL-TVP-10 states that four ISs 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 IS for the TST method. The next revision of the procedure will reflect this change.

5. The following deviation from procedure PNL-TVP-03 was noted. The compound hexane was not analyzed as a target compound in these samples because a proper standard was not available at the time of analysis. For this analysis, hexane was treated as a TIC when present. This provided a somewhat less accurate measure of the actual concentration of hexane because it was quantified using the response factor of the nearest eluting IS rather than the relative response factor generated from authentic standards. The compound will be added back to the target compound list as soon as the standard becomes available.

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 U-204 on 8/8/95.

Target Analytes	CAS No.	Mol Wt	Ret Time	S5037-A05.621[c] PNL 621[e] (mg/m³)	(ppbv)	S5037-A06.622[c][d] PNL 622[d][e] (mg/m³)	(ppbv)	S5037-A07.623[c] PNL 623[e] (mg/m³)	(ppbv)	Mean and Standard Deviations (mg/m³)	St Dev	(ppbv)	St Dev
Dichlorodifluoromethane	75-71-8	120.9		<0.03	< 5	0.04	7	0.02	3	0.03	(g)	5	(g)
Trichlorofluoromethane	75-69-4	137.4		3.36	547	3.62	590	3.56	581	3.51	0.14	573	22.6
Methylene Chloride	75-09-2	84.9		0.02	5	0.03	8	0.02	5	0.02	0.01	6	1.6
Carbon Tetrachloride	56-23-5	153.8		0.04	5	0.04	6	0.04	6	0.04	0.00	6	0.3
1-Butanol	71-36-3	74		0.04	11	<0.02	< 5	<0.02	< 5	(g)	(g)	(g)	(g)
Tentatively Identified Compound[f]													
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	6.5	<0.04	<10	0.07	15	0.09	20	0.60	(g)	18	(g)
Dibutyl butanephosphonate	78-46-6	250	58.5	<0.11	<10	<0.11	<10	<0.11	<10	(g)	(g)	(g)	(g)
Phosphoric acid tributyl ester	126-73-8	266	59.2	0.73	62	<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 U-204 on 8/8/95

				S5037-A06.622[c] PNL 622[d]		S5037-A06.622[c] PNL 622[d]		Relative Percent Difference
Target Analytes	CAS No.	Mol Wt		(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	%
Dichlorodifluoromethane	75-71-8	120.9		0.04	7	0.03	6	28.6
Trichlorofluoromethane	75-69-4	137.4		3.62	590	3.51	572	3.1
Methylene Chloride	75-09-2	84.9		0.03	8	0.02	5	40.0
Carbon Tetrachloride	56-23-5	153.8		0.04	6	0.04	6	0.0
1-Butanol	71-36-3	74.0		<0.02	< 5	<0.02	< 5	
Tentatively Identified Compound[e]								
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	6.5	0.07	15	0.15	33	74.7
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.

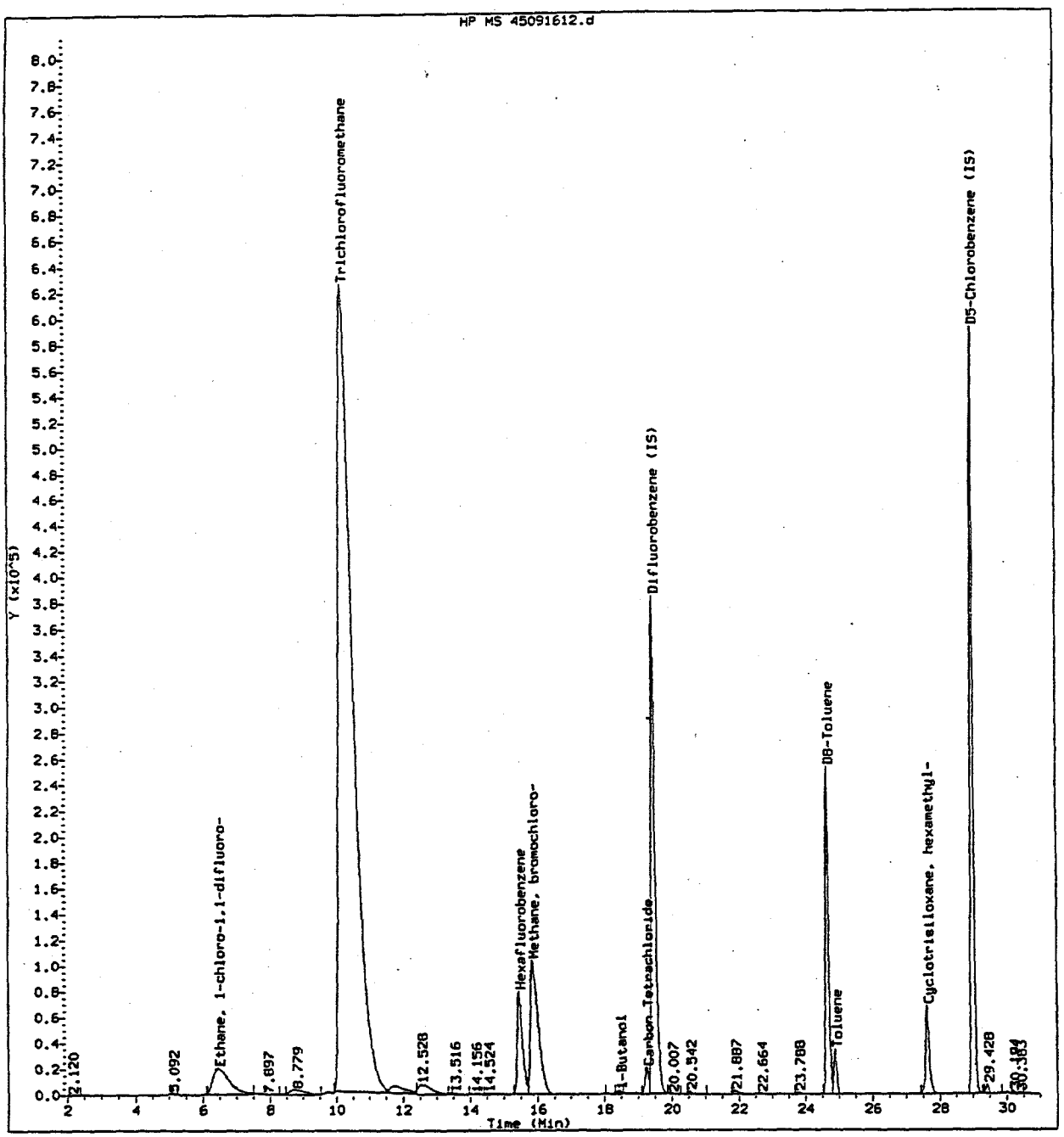

Figure E.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank U-204 Triple Sorbent Trap Sample S5037-A06-622 Collected on 8/8/95

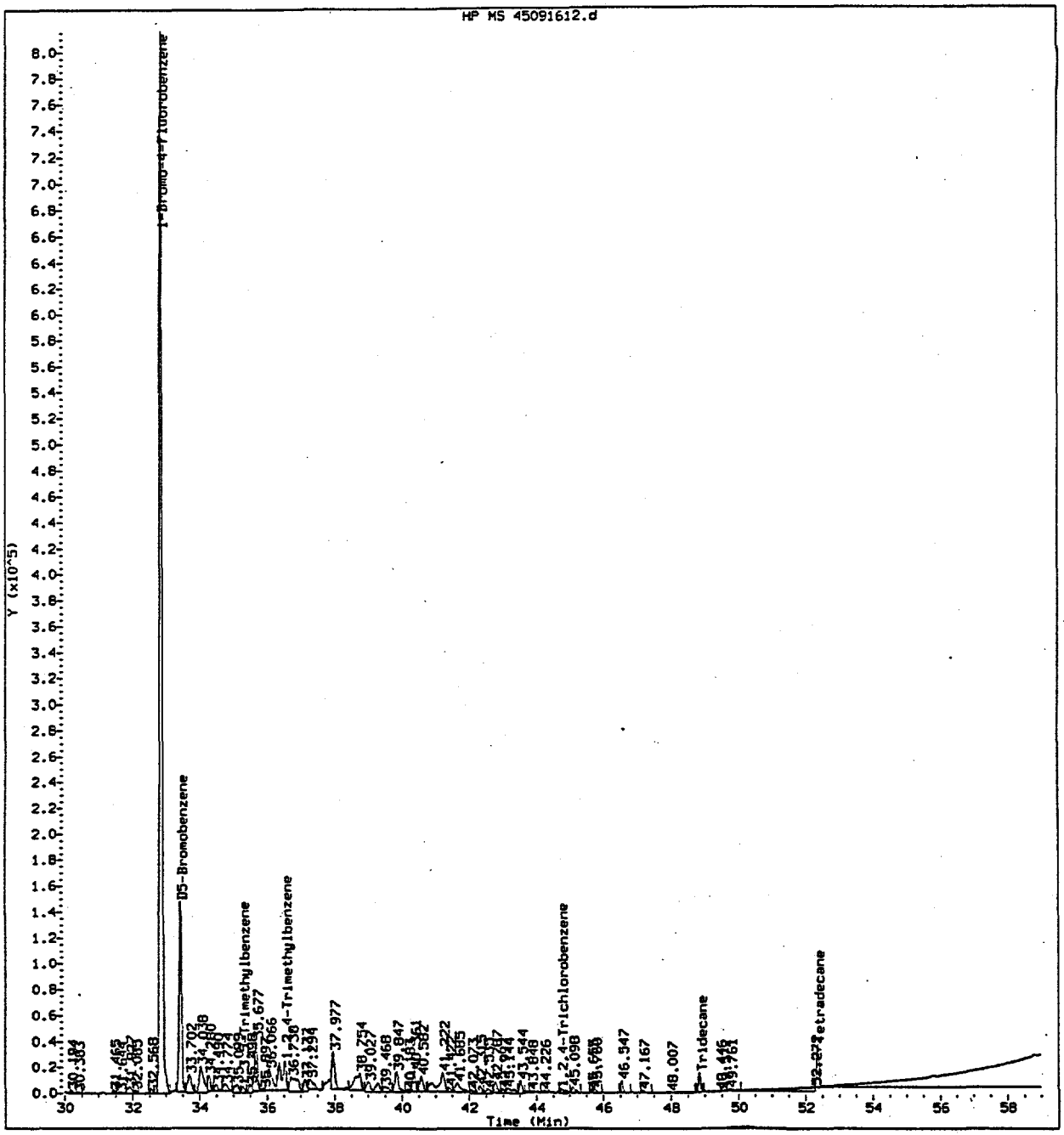

Figure E.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank U-204 Triple Sorbent Trap Sample S5037-A06-622 Collected on 8/8/95

Appendix F

Tank Vapor Characterization:

Chain-of-Custody Sample Control Forms

Battelle Pacific Northwest Laboratory	CHAIN OF CUSTODY	WHC 009247

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-U-204 Tank, Vapor Sample SAF S5037 (VSS Truck)

Collection date: 08 - 8 - 95
Preparation date: 08 - 01 - 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

S5037 - A08 . 55T	$NH_3/NO_x/H_2O$	(INORG Sorbent Trap # 1)
S5037 - A09 . 56T	$NH_3/NO_x/H_2O$	(INORG Sorbent Trap # 2)
S5037 - A10 . 57T	NO_x/H_2O	(INORG Sorbent Trap # 3)
S5037 - A11 . 58T	$NH_3/H_2O/H_2O$	(INORG Sorbent Trap # 4)
S5037 - A16 . 59T	$NH_3/NO_x/H_2O$	(INORG Sorbent Trap # 5)
S5037 - A17 . 60T	$NH_3/NO_x/H_2O$	(INORG Sorbent Trap # 6)
S5037 - A18 . 61T	NO_x/H_2O	(INORG Sorbent Trap # 7)
S5037 - A19 . 62T	$NH_3/H_2O/H_2O$	(INORG Sorbent Trap # 8)
S5037 - A25 . 63T	$NH_3/NO_x/H_2O$	(INORG Field Blank # 1)
S5037 - A26 . 64T	$NH_3/NO_x/H_2O$	(INORG Field Blank # 2)
S5037 - A27 . 65T	$NH_3/NO_x/H_2O$	(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	08-03-95	1145	J A Edwards	08-03-95	1145
J A Edwards	08-03-95	1350	T B Utecht	08-03-95	1350
T B Utecht	08-04-95	0700	R D Mahon	08-04-95	0700
R D Mahon	08-14-95	0730	T B Utecht	08-14-95	0730
T B Utecht	08-14-95	0930	J A Edwards	8-14-95	0930
J A Edwards	8-15-95	1400	G W Dennis	8-15-95	1400
G W Dennis	8-16-95	1515	K H Poole	8-16-95	1515

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	POC	

(Revised 05/10/95 PNL)

A-6000-407 (12/92) WEF061

Battelle Pacific Northwest Lab	CHAIN OF CUSTODY	WHC 009245

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-U-204 Tank Vapor Sample SAF S5037 (VSS Truck)	Collection date	08 - 8 - 95
		Preparation date	08 - 01 - 95
Ice Chest No.		Field Logbook No.	WHC-N-6470
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

S5037 - A01 . 014	Ambient Air SUMMA #1 Upwind of U-203
S5037 - A02 . 023	Ambient Air SUMMA #2 Through Port # 15
S5037 - A04 . 115	SUMMA #3 Port # 15
S5037 - A12 . 118	SUMMA #4 Port # 15
S5037 - A20 . 121	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	08-03-95	1330	T B Utecht T.B. Utecht	08-03-95	1330
T.B. Utecht / T.B. Utecht	08-08-95	0700	RD Mahon / RD Mahon	08-09-95	0700
RD Mahon / RD Mahon	08-14-95	0730	T.B. Utecht / T.B. Utecht	08-14-95	0730
T.B. Utecht / T.B. Utecht	08-14-95	0915	JA Edwards / JA Edwards	8-14-95	0915

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	POC	

(Revised 10/17/94 PNL)

A-6000-407 (12/92) WEF061

Battelle Pacific Northwest Laboratory	CHAIN OF CUSTODY	WHC 009246

Custody Form Initiator: J. A. Edwards - PNL
Telephone (509) 373-0141
Page 85-3009 / P8-08 / FAX 376-0418

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

Project Designation/Sampling Locations: 200 West Tank Farm
241-U-204 Tank Vapor Sample SAF S5037 (VSS Truck)

Collection date 08 - 8 - 95
Preparation date 07 - 20 - 95

Ice Chest No.

Field Logbook No. WHC-N-647-10

Ertco Hi/Lo thermometer No. PNL-T-003

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment: Government Truck

Shipped to: WHC

Possible Sample Hazards/Remarks: Unknown at time of sampling

Sample Identification

S5037 - A05 . 621	PNL Triple Sorbent Trap (TST) Sample # 1	
S5037 - A06 . 622	PNL TST Sample # 2	
S5037 - A07 . 623	PNL TST Sample # 3	
S5037 - A13 . 624	PNL TST Sample # 4	
S5037 - A14 . 625	PNL TST Sample # 5	
S5037 - A15 . 626	PNL TST Sample # 6	
S5037 - A21 . 627	Open, close & store PNL TST Field Blank # 1	In VSS truck
S5037 - A22 . 628	Open, close & store PNL TST Field Blank # 2	In VSS truck
S5037 - A23 . 629	Store PNL TST Trip Blank # 1	None
S5037 - A24 . 630	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 / J A Edwards	08-03-95	1330	T B Utecht / T B Utecht	08-03-95	1330
T.B. Utecht / T.B. Utecht	08-04-95	0700	R D Mahon / R D Mahon	08-04-95	0700
R D Mahon / R D Mahon	08-14-95	0730	T B Utecht / T B Utecht	08-14-95	0730
T.B. Utecht / T.B. Utecht	08-14-95	0920	J A Edwards / J A Edwards	8-14-95	0920

Final Sample Disposition

Comments:

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

Comments:

Cooler Temperature Status

Hi -15 °C / Lo -15 °C (pick up at PNL to WHC)
Hi 6 °C / Lo 5 °C (delivery at WHC from PNL)
Hi ___ °C / Lo ___ °C (at return to PNL from WHC)
Hi 3 °C / Lo 3 °C (at delivery from WHC to PNL)

(Revised 06/21/95 PNL)

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