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Tank Vapor Characterization Project

Headspace Vapor Characterization of Hanford Waste Tank AX-102: Results from Samples Collected on 6/27/95

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November 1995

**Prepared for Westinghouse Hanford Company
under a Related Services Agreement
with the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy**



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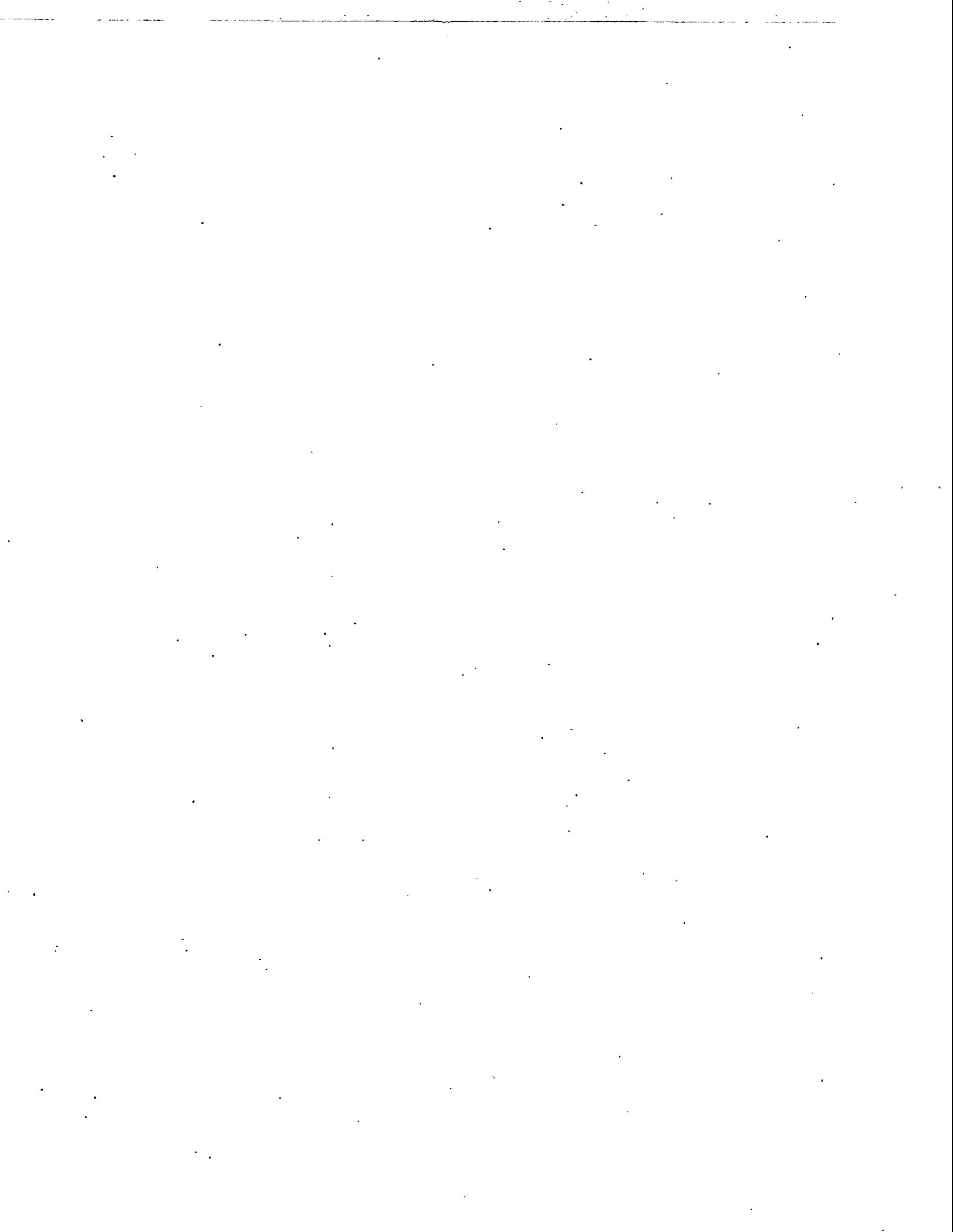
Summary

This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-AX-102 (Tank AX-102) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support safety evaluations and tank-farm operations. The results include air concentrations of selected inorganic and organic analytes and grouped compounds from samples obtained by Westinghouse Hanford Company (WHC) and provided for analysis to Pacific Northwest National Laboratory (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 AX-102 on 6/27/95

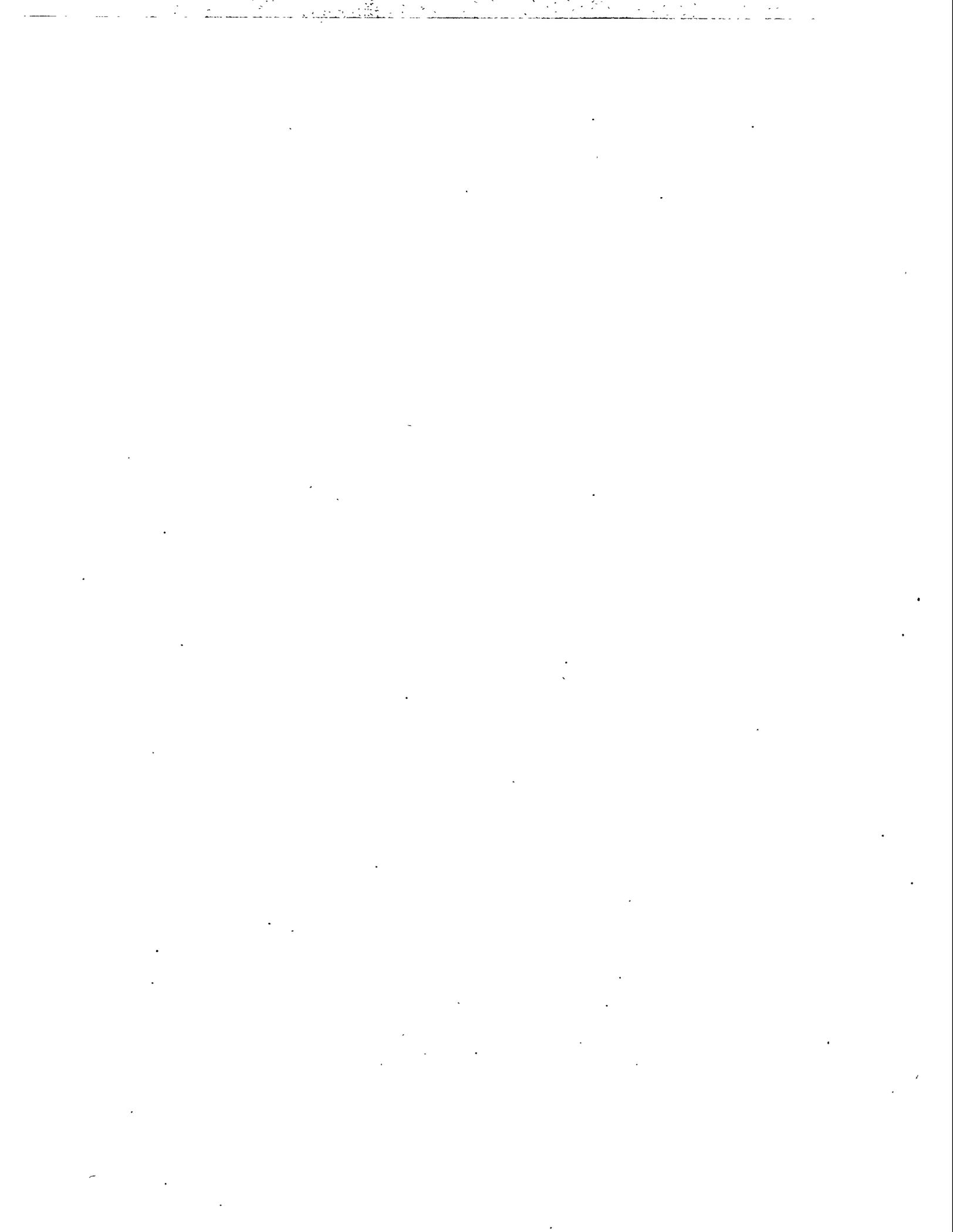
<u>Category</u>	<u>Sample Medium</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic Analytes	Sorbent Traps	NH ₃	34 ± 3	ppmv
		NO ₂	≤ 0.08	ppmv
		NO	0.18 ± 0.03	ppmv
		H ₂ O	13.4 ± 0.6	mg/L
Permanent Gases	SUMMA™ Canister	CO ₂	704	ppmv
		CO	<12	ppmv
		CH ₄	<12	ppmv
		H ₂	<98	ppmv
		N ₂ O	50	ppmv
Volatile Organics (TO-14)	SUMMA™ Canister	Methyl Alcohol	4.01	mg/m ³
		Trichlorofluoromethane	2.49	mg/m ³
		3-Heptanone	1.17	mg/m ³
Semi-Volatile Organics (PNL-TVP-10)	Sorbent Traps	Trichlorofluoromethane	1.54	mg/m ³
		3-Heptanone	1.28	mg/m ³
		1-Butanol	0.52	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 Appendices A through E.



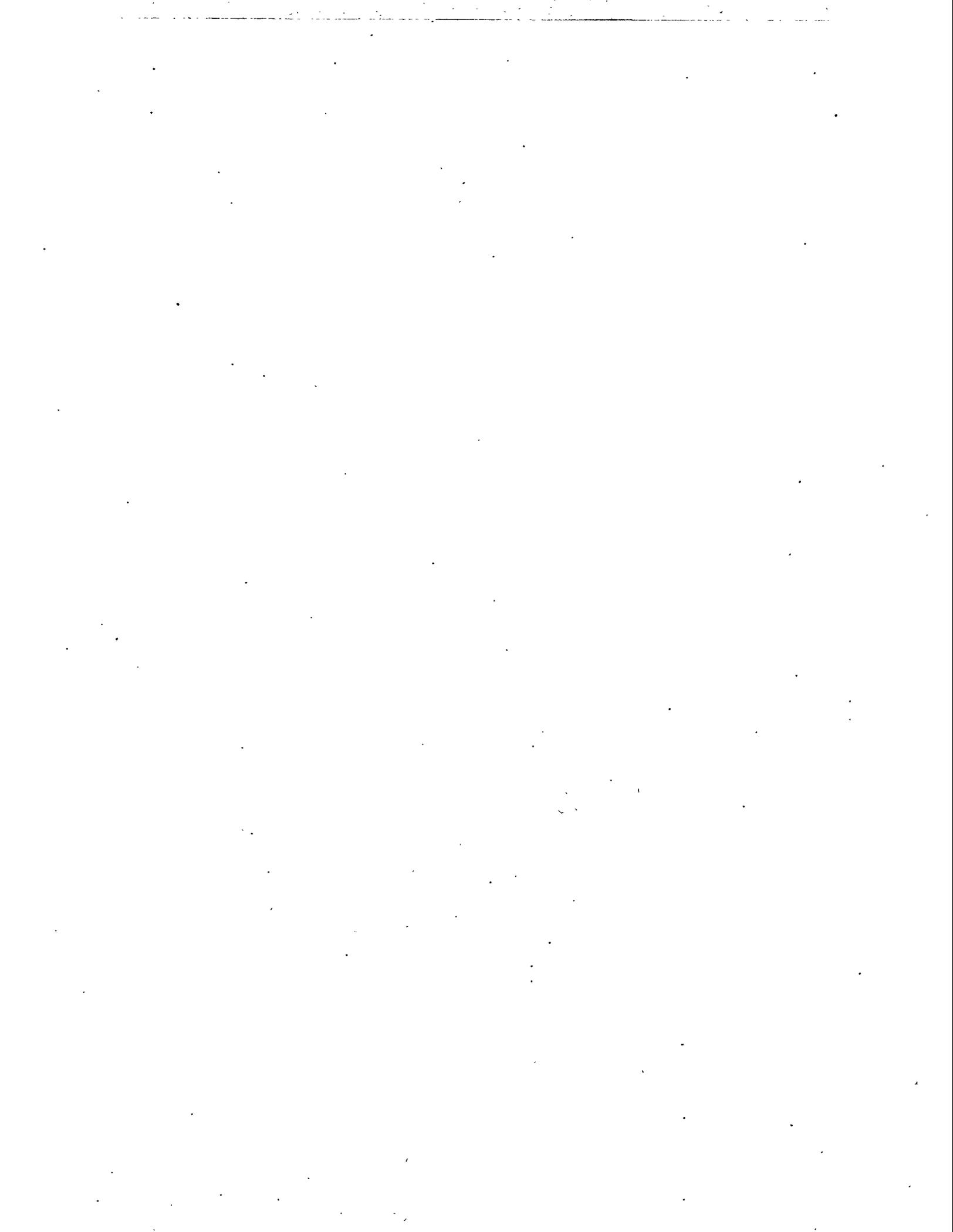
Acknowledgments

The authors gratefully acknowledge the support of other project staff at Pacific Northwest National Laboratory (PNL) who contributed to the successful completion of this sampling and analysis activity. J. A. Edwards served as the PNL single-point-of-contact for sample preparation and shipping. J. L. Julya assisted with organic laboratory work. S. O. Slate, K. P. Schielke, L. M. P. Thomas, and G. W. Dennis supported inorganic laboratory work.



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-AX-102 (Tank AX-102) 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 S5035. Samples were collected by WHC on June 27, 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 12 sorbent trains for selected inorganic analytes (6 sample trains and 6 trip and field blanks), 5 SUMMA™ canisters for permanent gases and volatile organic analytes (3 sample and 2 ambient canisters), and 16 triple sorbent traps (TSTs) for semi-volatile organic analytes (12 sample and 4 control traps). The samples and controls were provided to WHC on May 31, 1995. Exposed samples and controls were returned to PNL on June 29, 1995. Samples and controls were handled, stored, and transported using chain-of-custody (COC) forms to ensure that sample quality was maintained.

Samples and controls were handled and stored as per 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 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 AX-102 on 6/27/95 (Sample Job S5035) 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 34 ± 3 ppmv (NH_3), ≤ 0.08 ppmv (NO_2), 0.18 ± 0.03 ppmv (NO), and 13.4 ± 0.6 mg/L (primarily H_2O). The vapor concentration results were based on six samples for each compound. The NO_2 and NO samples were located downstream of NH_3 sorbent traps during the sample job. All samples (100%) were successfully analyzed and used in the averages. Representative field blanks were also analyzed and used to correct data. Two of the four average concentration results (for NH_3 and H_2O) exceeded the minimum of the expected ranges. The precision of results, based on one standard deviation of all samples, was $\leq \pm 9\%$ (within the target level of $\pm 25\%$) for analytes exceeding expected ranges (the precision of the NO sample results was $\pm 16\%$; however, the result [0.18 ppmv] was less than the expected range of 2 ppmv). 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 levels. The estimated uncertainty range was slightly exceeded by one control spike of an NH_3 sample, which indicated a percentage recovery of 112%. As this was within the target range, no action was taken. Evaluating the variability of field blanks (H_2O) indicated water vapor results were within required accuracy limits. No procedural deviations were noted, however, minor ($\leq 20\%$) trends in NH_3 and H_2O samples indicated a potential sampling issue (Appendix A.4.1 and A.4.3). Data and additional information on samples, analyses, and results are described in Appendix A. The COC form used to control samples, 008897, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent-gas analysis of Tank AX-102 can be found in Appendix B of this report. In summary, carbon dioxide at 704 ppm and nitrous oxide at 50 ppm were observed in the tank-headspace samples.

2.3 Total Non-Methane Hydrocarbons

The Tank AX-102 samples were not analyzed for TO-12 analytes.

2.4 Volatile Organic Analytes

The complete results of the TO-14 analysis of Tank AX-102 can be found in Appendix D of this report. In summary, 9 target analytes above the 5-ppbv reporting cutoff and 18 TICs above the 10-ppbv reporting cutoff were detected in the tank-headspace samples. Eight of 18 TICs were identified as unknowns. The total concentration of the target analytes was found to be 4.36 mg/m³. The total TIC concentration was found to be 5.54 mg/m³. The total concentration of all the compounds identified was 9.90 mg/m³. SUMMA™ canister PNL 218 was analyzed in replicate for target analytes and TICs to determine analytical precision. Seven of 9 target analytes and 10 of 17 TICs had relative percent differences (RPDs) of less than 10%. Acetone was observed in the ambient-air samples and the ambient air through the VSS sample. No TICs were observed in the two ambient-air samples.

2.5 Semi-Volatile Organic Analytes

The complete results of the sorbent-trap analysis of Tank AX-102 can be found in Appendix E of this report. In summary, 11 target analytes above the 5-ppbv reporting cutoff and 30 TICs above the 10-ppbv reporting cutoff were detected in the tank-headspace samples. All the target analytes and 29 of 30 TICs were observed in two or more sorbent traps. Ten of 30 TICs were identified as unknowns. The total concentration of the target analytes was found to be 3.29 mg/m³. The total concentration of the TICs was found to be 4.59 mg/m³. The total concentration of all the compounds identified was 7.89 mg/m³. Triple-sorbent-trap sample PNL 506 was analyzed in replicate for target analytes and TICs to determine analytical precision. All 11 target analytes and 14 of 28 TICs had RPDs of less than 10%.

The TST procedure is relatively new. Tank AX-102 was the third tank analyzed by the newly developed method PNL-TVP-10, which was being finalized as a parallel effort during the same time period. A thorough examination of procedural issues has not revealed any significant issues affecting data quality. A 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 9 target analytes and 6 TICs that were common to both analyses. Seven of 15 compounds were higher in the TST versus the SUMMA™ samples. Of particular interest for comparison were the low-volatility compounds, such as dodecane, tridecane, and tetradecane, which were observed at moderate levels in the TST, but were absent from the SUMMA chromatograms. This same trend has been observed in earlier analyses, particularly Tank A-101. The TST method is apparently more representative for the less

volatile analytes. Well identified compounds in the mid-volatility range, such as 2-butanone, 1-butanol, butanenitrile, heptane, tetrachloroethene, 3-heptanone, 2-heptanone, and 4-heptanone, tended to give essentially equivalent results by both methods. The most volatile compounds, such as methanol, butane, acetonitrile, and trichlorofluoromethane, tended to be somewhat higher by the SUMMA™ method. The TST method tended to also show a more diverse collection of TICs, many of which were not reported by the SUMMA™ method. For most of the compounds showing common detection by both methods, the TST method generally exhibited better precision than the SUMMA™ method for duplicate and repeat analyses.

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 SUMMATM Canister Collected from the Headspace of Tank AX-102 on 6/27/95

Target Analytes	CAS No.	S5035 ^(c) TST Results		S5035 ^(c) SUMMA TM Results		Relative Percent Difference
		(mg/m ³)	St Dev	(mg/m ³)	St Dev	%
Acetonitrile	75-05-8	0.28	0.00	0.48	0.06	-53
Acetone	67-64-1	0.43	0.03	0.58	0.06	-30
Trichlorofluoromethane	75-69-4	1.54	0.01	2.49	0.24	-47
Methylene Chloride	75-09-2	0.02	0.01	<0.02		na
Propanenitrile	107-12-0	0.17	0.02	0.11	0.01	43
Propanol	71-23-8	0.14	0.01	0.07	0.01	69
2-Butanone	78-93-3	0.17	0.01	0.14	0.02	20
Butanenitrile	109-74-0	0.26	0.00	0.27	0.02	-4
Heptane	142-82-5	0.06	0.00	0.05	0.01	25
Toluene	108-88-3	0.02	0.00	<0.02		na
Tetrachloroethylene	127-18-4	0.19	0.01	0.18	0.01	6
Tentatively Identified Compounds^(b)						
Propane	74-98-6	<0.02		0.24	0.02	na
Methyl Alcohol	67-56-1	0.42	0.05	4.01	0.38	-162
Butane	106-97-8	0.05	0.01	0.28	0.03	-142
Methane, dichlorofluoro-	75-43-4	<0.05		0.25	0.04	na
Ethanol	64-17-5	0.12	(d)	0.47	0.24	-121
1-Propanol	71-23-8	0.10	0.03	<0.03		na
Butanal	123-72-8	0.07	0.04	0.22	0.02	-101
1-Butanol	71-36-3	0.52	0.01	0.39	0.03	28
Propylene Glycol	57-55-6	0.14	0.01	<0.03		na
Pentanenitrile	110-59-8	0.06	0.02	<0.04		na
2-Hexanone	591-78-6	0.05	(d)	<0.04		na
Heptane, 3-methyl-	589-81-1	0.08	0.00	<0.05		na
Nitric acid, butyl ester	928-45-0	0.06	0.01	<0.05		na
3-Heptanone	106-35-4	1.28	0.03	1.17	0.16	9
3-Heptanol	589-82-2	0.13	0.00	<0.05		na
Butanamide	541-35-5	0.08	0.02	<0.04		na
Hexanal, 2-ethyl-	123-05-7	0.11	0.01	<0.06		na
1-Hexanol, 2-ethyl-	104-76-7	0.14	0.01	<0.06		na
Dodecane	112-40-3	0.08	0.00	<0.08		na
Tridecane	629-50-5	0.22	0.00	<0.08		na
Tetradecane	629-59-4	0.09	0.00	<0.09		na

(a) TO-14 plus 14 additional target analytes.

(b) Semi-quantitative estimate calculated using concentration of closest eluting internal standard

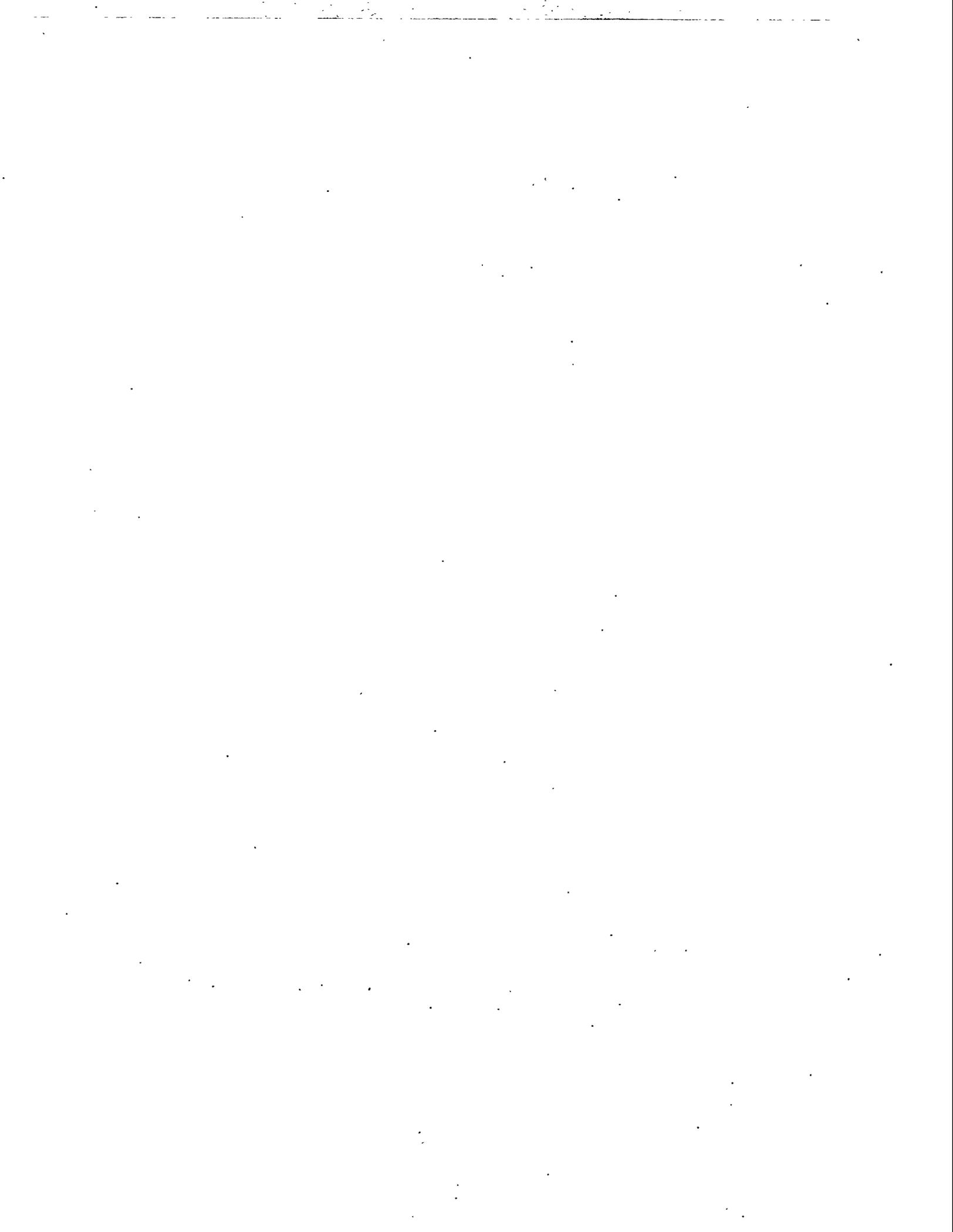
(c) WHC sample job number.

(d) Standard deviation not applicable; Compound observed above MDL in only two SUMMATM or Triple Sorbent Trap Samples

na Not applicable

3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank AX-102 on June 27, 1995 (Sample Job S5035). 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 (supplied by SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for vapor sampling. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration to perform workplace monitoring and because of available procedures and verification results associated with that particular application. The typical sorbent traps used consisted of a glass tube containing a sorbent material specific to the compound of interest. In general, the tubes contained 2 sorbent layers, or sections; the first layer was the primary trap, and the second layer provided an indication of breakthrough. In the tubes, sorbent layers are generally held in packed layers separated by glass wool. The sorbent traps, having glass-sealed ends, were received from the vendor.

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

(a) Pacific Northwest Laboratory. 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 ≤ 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 NH₃ equals

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

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

A.2 Analytical Procedures

The compounds of interest were trapped using solid sorbents and chemisorption (adsorption of water vapor). Analytical results were based on extraction and analysis of selected ions. Analytical procedures used are specified in the text. 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- $\mu\text{g}/\text{mL}$ (ppm) NH_3 stock standard solution from dried reagent-grade NH_4Cl and DIW, 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm NH_3 working calibration standards by serial dilution of the freshly made stock standard, 3) generating an initial calibration curve from the measured electromotive force signal versus NH_3 concentration data obtained for the set of working standards, 4) performing a calibration-verification check, using a mid-range dilution of a certified National Institute for Standards and Technology (NIST)-traceable 0.1 M NH_4Cl standard from an independent source, after analyzing every 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 $1 \mu\text{g/mL}$ or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Working standards are traceable to NIST-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)

<u>Analyte</u>	<u>Formula</u>	<u>Procedure</u>	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	$\geq 3 \text{ mg/L}$	n/a

- (a) Analytical precision and accuracy targets for results in the expected ranges equal $\pm 25\%$ and 70 to 130%, respectively (Osborne et al. 1995).
- (b) 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 NH₃ and 3 mL for NO and NO₂. 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 $\pm 0.1 \text{ mg}$, 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 $\pm 1 \text{ mg}$ per 5-trap sorbent train.

A.4 Inorganic Sample Results

Samples were obtained by WHC from the tank headspace of Tank AX-102 on 6/27/95 using the VSS. The sample job designation number was S5035. 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 NH₃, NO₂, NO, and mass (primarily H₂O). Samples were controlled using chain-of-custody 008897 (Appendix F). The inorganic samples were received from WHC on 6/29/95; the sample-volume information was received on 7/5/95. Analyses were completed on 7/11/95 (gravimetric, 14 day hold time), 7/14/95 (ammonia, 17 day hold time), and 7/14/95 (nitrite, 17 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 NH₃/NO_x/H₂O contained an NH₃ 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 34 ± 3 ppmv, based on all six samples. Sample results indicated a potentially increasing trend in concentration of roughly 20% with increasing sample port number (see Tables A.2 and A.3); such an increase was also seen to a lesser extent in the gravimetric results (Section A.4.3). The blank-corrected NH_3 quantities in the sorbent traps ranged from 4.0 to 4.9 μmol in front sections and were about 0.05 μmol in back sections. Blank corrections, ≤ 0.08 μmol in front and ≤ 0.05 μmol in back sections, were about 1.7% of collected quantities. The analyses of two samples were duplicated and yielded repeatabilities of ± 3 and $\pm 5\%$. One sample leachate was spiked after initial analysis with roughly the quantity of NH_3 in the sample and yielded a percentage recovery of 112%. The continuing calibration verification standard, using NIST-traceable material, yielded percentage recoveries of 98 and 107% during the analytical session. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 $\mu\text{g}/\text{mL}$. Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol NH_3 were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively, during previous sample jobs (Clauss et al. 1994; Ligothke et al. 1994).

A.4.2 Nitrogen Oxides Results. Measurements of NO_2 and NO were made using six 5-segment $\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ sorbent-trap trains (the NO_x trains consisted of NO_2 trap, oxidizer, NO_2 trap). Related sample jobs, performed using the VSS in BY-104, -105, and -106 both with and without NO_x trains protected by a leading NH_3 trap (e.g., Clauss et al. 1994), indicated that the presence of the upstream NH_3 traps resulted in NO concentrations that were about 1.3- to 1.6-fold less than those from unprotected NO_x traps. The NO_2 concentrations were also potentially less following an NH_3 trap.

The concentrations of NO_2 and NO were ≤ 0.08 and 0.18 ± 0.03 ppmv, respectively, based on all six samples. Blank-corrected NO_2^- quantities in the sorbent traps averaged ≤ 0.0053 μmol (NO_2 samples) and 0.0117 μmol (NO samples). Nitrite blank levels used to correct data were 0.0124 ± 0.0012 μmol in front (6 of 12 blanks analyzed) and 0.0069 ± 0.0013 μmol in back (4 of 12 blanks analyzed) sorbent sections. The analyses of two samples were duplicated, and each yielded a repeatability of $\pm 2\%$. Two sample leachates were spiked with 0.25 ppm NO_2^- and yielded percentage recoveries of 95 and 105%. 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 $153 \pm 14\%$, $103 \pm 4\%$, $106 \pm 8\%$, and $111 \pm 7\%$, respectively (Clauss et al. 1994; Ligothke 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 AX-102 on 6/27/95

<u>Sample Number</u>	<u>Sorbent Type</u>	<u>Sample Port and Volume Information^(a)</u>				
		<u>Sample Port</u>	<u>Flow Rate (mL/min)</u>	<u>Duration (min)</u>	<u>Volume (L)</u>	<u>Mass Gain (g)</u>
<u>Samples:</u>						
S5035-A23-U36	NH ₃ /NO _x /H ₂ O Train	1	200	15.0	3.00	0.0451
S5035-A24-U37	NH ₃ /NO _x /H ₂ O Train	2	200	15.0	3.00	0.0459
S5035-A25-U38	NH ₃ /NO _x /H ₂ O Train	3	200	15.0	3.00	0.0474
S5035-A26-U39	NH ₃ /NO _x /H ₂ O Train	4	200	15.0	3.00	0.0480
S5035-A27-U40	NH ₃ /NO _x /H ₂ O Train	5	200	15.0	3.00	0.0485
S5035-A28-U41	NH ₃ /NO _x /H ₂ O Train	6	200	15.0	3.00	0.0497
<u>Controls:</u>						
S5035-A29-U42	NH ₃ /NO _x /H ₂ O Trip Blank	n/a ^(b)	n/a	n/a	n/a	0.0047
S5035-A30-U43	NH ₃ /NO _x /H ₂ O Trip Blank	n/a	n/a	n/a	n/a	0.0048
S5035-A31-U44	NH ₃ /NO _x /H ₂ O Trip Blank	n/a	n/a	n/a	n/a	0.0053
S5035-A32-U45	NH ₃ /NO _x /H ₂ O Field Blank	n/a	n/a	n/a	n/a	0.0059
S5035-A33-U46	NH ₃ /NO _x /H ₂ O Field Blank	n/a	n/a	n/a	n/a	0.0070
S5035-A34-U47	NH ₃ /NO _x /H ₂ O Field Blank	n/a	n/a	n/a	n/a	0.0083

(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 5-trap sorbent trains, believed to be primarily water vapor, was 13.4 ± 0.6 mg/L. Sample results indicated a potentially increasing trend in concentration of roughly 10% with increasing sample port number (see Tables A.2 and A.3); such an increase was also seen to a greater extent in the NH₃ results (Section A.4.1). The result was based on an average mass gain of 40.3 mg from all six NH₃/NO₂/H₂O sample trains. The blank correction applied to the results was - 7.1 mg per train, based on a mass gain of 7.1 ± 1.2 mg per three field-blank 5-trap sorbent trains. Although no spiked blanks were tested, the percentage recovery of mass from three blank H₂O traps spiked with 51 mg of water was $103 \pm 2\%$ during a previous sample job (Clauss et al. 1994).

Table A.3 Inorganic Vapor Sample Results Obtained from a Heated Tube Inserted into the Headspace of Tank AX-102 on 6/27/95

<u>Sample</u>	<u>Analytical Results (μmol)</u>			<u>Sample Volume (L)</u>	<u>Vapor^(a) Concentration (ppmv)</u>
	<u>Front Section</u>	<u>Back Section</u>	<u>Total^(b) Blank-Corrected</u>		
<u>NH₃ Samples:</u>			<u>4.53^(c)</u>	<u>3.00^(c)</u>	<u>34 ± 3^(c)</u>
S5035-A23-U36	4.07	NA ^(d)	3.99	3.00	30
S5035-A24-U37	4.41	0.05	4.33	3.00	32
S5035-A25-U38	4.57	NA	4.49	3.00	34
S5035-A26-U39	4.79	0.04	4.71	3.00	35
S5035-A27-U40	4.99	NA	4.91	3.00	37
S5035-A28-U41	4.85	0.05	4.77	3.00	36
<u>NO₂ Samples:</u>			<u>≤ 0.0053</u>	<u>3.00</u>	<u>≤ 0.08</u>
S5035-A23-U36	0.0143	0.0067	n/a ^(d)	3.00	n/a
S5035-A24-U37	0.0146	0.0064	n/a	3.00	n/a
S5035-A25-U38	0.0137	NA	n/a	3.00	n/a
S5035-A26-U39	0.0137	NA	n/a	3.00	n/a
S5035-A27-U40	0.0141	NA	n/a	3.00	n/a
S5035-A28-U41	0.0182	NA	n/a	3.00	n/a
<u>NO Samples:</u>			<u>0.0117</u>	<u>3.00</u>	<u>0.18 ± 0.03</u>
S5035-A23-U36	0.0252	NA	0.0128	3.00	0.19
S5035-A24-U37	0.0229	NA	0.0105	3.00	0.16
S5035-A25-U38	0.0256	NA	0.0132	3.00	0.20
S5035-A26-U39	0.0212	NA	0.0088	3.00	0.13
S5035-A27-U40	0.0255	0.0065	0.0131	3.00	0.20
S5035-A28-U41	0.0239	0.0060	0.0115	3.00	0.17
<u>Gravimetric Samples:</u>			<u>40.3 mg</u>	<u>3.00</u>	<u>13.4 ± 0.6 mg/L</u>
S5035-A23-U36	n/a	n/a	38.0	3.00	12.7
S5035-A24-U37	n/a	n/a	38.8	3.00	12.9
S5035-A25-U38	n/a	n/a	40.3	3.00	13.4
S5035-A26-U39	n/a	n/a	40.9	3.00	13.6
S5035-A27-U40	n/a	n/a	41.4	3.00	13.8
S5035-A28-U41	n/a	n/a	42.6	3.00	14.2

- (a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (Table 2.2). 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 NO₂ and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The level of analytes found in blanks is described in the subsections of Section 2.4.
- (c) Underlined values represent the average of the set samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. The use of " \leq " is defined in Section 2.4.
- (d) NA = not analyzed; n/a = not applicable. Only selected back sorbent sections were analyzed. Past results have shown back sections of NH₃ samples to contain insignificant quantities of the analyte.

A.5 References

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

Ligothke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94 - 5/25/94)*. PNL-10172, Pacific Northwest 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, 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 (H₂), carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), and nitrous oxide (N₂O), by gas chromatograph/thermal conductivity detection (GC/TCD). Aliquots of sampled air are drawn directly from each canister into a 5-mL gas-tight syringe and injected into a Hewlett-Packard 5890 GC/TCD fitted with a loop injector valve and a column switching valve. An aliquot of 5 mL is used so that the 1.0-mL injection loop is completely purged with sample air, ensuring that no dilution of the sample takes place within the injection loop. One set of GC conditions is used to analyze for CO, CO₂, N₂O, and CH₄ using Helium (He) as the carrier gas. A second GC analysis is performed for H₂ (using nitrogen as the carrier gas) to enhance the signal sensitivity and lower the detection limit for this analyte. The permanent gases and the derived method detection limit (MDL) are listed in Table B.1.

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

<u>Analyte</u>	<u>Formula</u>	<u>Procedure</u>	<u>MDL (ppmv)</u>
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 ₂ O	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, CO₂, N₂O, and CH₄ 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 H₂, except the carrier gas was changed to N₂. A least-squares linear-regression routine was applied to the calibration data set to generate the best line fit for each compound.

Each analyte was quantitated by direct comparison of sample analyte peaks to the calibration plot generated for the compound. The lowest calibration standard for each analyte is reported as the MDL. An MDL for the instrument has not been determined. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within $\pm 25\%$ of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N₂ reagent blank, an ambient-air sample collected ~10 m upwind of Tank AX-102, 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 AX-102, ambient air collected ~10 m upwind of the tank, and ambient air collected through the vapor sampling system. The samples were analyzed on June 30, 1994. Carbon dioxide at 704 ppm and nitrous oxide at 50 ppm were observed in the tank-headspace samples. Carbon dioxide in the headspace was at a higher concentration than observed in the ambient air. A replicate analysis was performed on SUMMA™ canister PNL 218; 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 AX-102 and for Ambient Air and Ambient Air Through the VSS Collected Near Tank AX-102 in SUMMA™ Canisters on 6/27/95

<u>Sample</u>	<u>Sample Matrix</u>	<u>PNL Canister Number</u>	<u>Sample Concentration (ppmv)</u>	<u>Average Concentration (ppmv)^(a)</u>
<u>CO_x Samples:</u>				
S5035-A04-212	Tank	212	698	704
S5035-A05-218	Tank	218	705	
S5035-A06-220	Tank	220	710	
S5035-A05-218	Tank ^(b)	218	707	
S5035-A01-257	Ambient Air - Upwind	257	330	
S5035-A02-258	Ambient Air - VSS	258	334	
<u>CO Samples:</u>				
S5035-A04-212	Tank	212	<12	<12
S5035-A05-218	Tank	218	<12	
S5035-A06-220	Tank	220	<12	
S5035-A05-218	Tank ^(b)	218	<12	
S5035-A01-257	Ambient Air - Upwind	257	<12	
S5035-A02-258	Ambient Air - VSS	258	<12	
<u>CH₄ Samples:</u>				
S5035-A04-212	Tank	212	<12	<12
S5035-A05-218	Tank	218	<12	
S5035-A06-220	Tank	220	<12	
S5035-A05-218	Tank ^(b)	218	<12	
S5035-A01-257	Ambient Air - Upwind	257	<12	
S5035-A02-258	Ambient Air - VSS	258	<12	
<u>H₂ Samples:</u>				
S5035-A04-212	Tank	212	<98	<98
S5035-A05-218	Tank	218	<98	
S5035-A06-220	Tank	220	<98	
S5035-A05-218	Tank ^(b)	218	<98	
S5035-A01-257	Ambient Air - Upwind	257	<98	
S5035-A02-258	Ambient Air - VSS	258	<98	
<u>N₂O Samples:</u>				
S5035-A04-212	Tank	212	50	50
S5035-A05-218	Tank	218	51	
S5035-A06-220	Tank	220	50	
S5035-A05-218	Tank ^(b)	218	52	
S5035-A01-257	Ambient Air - Upwind	257	<12.6	
S5035-A02-258	Ambient Air - VSS	258	<12.6	

- (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/m³ 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.

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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. 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.

All sequence analyses included the NIST 3-part per million by volume (ppmv) propane standard along with the appropriate blanks and 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/m³ 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/m³ was derived from the 5-point multilevel calibration curve from the propane standard using the following equation:

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

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

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

C.4 Total Non-Methane Hydrocarbons Sample Results

The SUMMA™ canister samples collected during this tank sampling event were not analyzed for TO-12 analytes.

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-Trichlorobenzene
cis-1,2-Dichloroethene	Hexachloro-1,3-butadiene
Chloroform	2-Butanone
1,2-Dichloroethane	Acetone
1,1,1-Trichloroethane	Acetonitrile
Benzene	Heptane
Carbon Tetrachloride	Tetrahydrofuran
1,2-Dichloropropane	Pyridine
Trichloroethene	Butanenitrile
cis-1,3-Dichloropropene	Cyclohexane
trans-1,3-Dichloropropene	Decane
1,1,2-Trichloroethane	Hexane
Toluene	4-Methyl-2-pentanone
1,2-Dibromoethane	Propanenitrile
Tetrachloroethylene	Cyclohexanone
Chlorobenzene	Propanol
Ethylbenzene	

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 met.

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-d₃, and bromofluorobenzene was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank-headspace samples are analyzed.

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

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

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

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

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

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

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

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 June 29, 1995, under Westinghouse Hanford Company (WHC) chain-of-custody 008898 (see Appendix F). The samples were analyzed on July 5, 1995.

The results from the GC/MS analysis of the tank-headspace SUMMA™ samples are presented in Table D.2. The results of replicate analyses on a single SUMMA™ canister are presented in Table D.3. The results of the GC/MS analysis of the ambient-air sample collected upwind of Tank AX-102 and through the VSS near Tank AX-102 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. Nine target analytes above the 5-ppbv reporting cutoff and 18 TICs above the 10-ppbv reporting cutoff were detected in the tank-headspace samples. Eight of 18 TICs were identified as unknowns. Trichlorofluoromethane ($2.49 \text{ mg}/\text{m}^3$), acetone ($0.58 \text{ mg}/\text{m}^3$), and acetonitrile ($0.48 \text{ mg}/\text{m}^3$) accounted for 81% of the target analytes and 35% of the total concentration identified by both the target and TIC analyses. Trichlorofluoromethane accounted for 57% of the total concentration of target analytes and 21% of the total concentration identified by both analyses. The total concentration of the target analytes was found to be $4.36 \text{ mg}/\text{m}^3$ or 44% of the total concentration identified by both the target and TIC analyses. The predominant TICs observed in these samples were methyl alcohol ($4.01 \text{ mg}/\text{m}^3$), 3-heptanone ($1.17 \text{ mg}/\text{m}^3$), and ethanol ($0.47 \text{ mg}/\text{m}^3$). Methyl alcohol, the highest

concentration TIC, accounted for 72% of the TIC concentration and 40% of the total concentration identified by both analyses. The total concentration of the TICs was found to be 5.54 mg/m³ or 56% of the total concentration identified by both the target and TIC analyses. The total concentration of target analytes and TICs was 9.90 mg/m³.

SUMMA™ canister PNL 218 was analyzed in replicate for target analytes and TICs to determine analytical precision. The relative percent difference (RPD) results are presented in Table D.3. The RPD was calculated for analytes detected above the detection limit and found in both replicates. Seven of the 9 target analytes and 10 of 17 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). Acetone was observed in the ambient-air sample and the ambient air through the VSS sample. 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 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.

Table D.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b), for Samples from the Headspace in Tank AX-102 in SUMMA™ Canisters collected on 6/27/95.

Target Analytes	CAS No.	Mol Wt	Ret Time	S5-035-A04.212 ^(c)		S5-035-A05.218 ^(c)		S5-035-A06.220 ^(c)		Mean and Standard Deviations			
				PNL 212 ^(e) (mg/m ³)	(ppbv)	PNL 218 ^(e) (mg/m ³)	(ppbv)	PNL 220 ^(e) (mg/m ³)	(ppbv)	(mg/m ³)	St Dev	(ppbv)	St Dev
Acetonitrile	75-05-8	41.1		0.42	228	0.48	262	0.54	294	0.48	0.06	261	32.8
Acetone	67-64-1	58.1		0.53	206	0.58	223	0.64	246	0.58	0.06	225	20.1
Trichlorofluoromethane	75-69-4	137.4		2.26	368	2.46	401	2.74	446	2.49	0.24	405	39.2
Propanenitrile	107-12-0	55.1		0.10	43	0.11	43	0.12	50	0.11	0.01	45	4.0
Propanol	71-23-8	60.1		0.07	27	0.06	24	0.08	28	0.07	0.01	26	2.5
2-Butanone	78-93-3	72.1		0.12	38	0.15	47	0.14	44	0.14	0.02	43	4.6
Butanenitrile	109-74-0	69.1		0.25	82	0.29	95	0.27	88	0.27	0.02	88	6.8
Heptane	142-82-5	100.2		0.05	11	0.05	12	0.04	10	0.05	0.01	11	1.1
Tetrachloroethylene	127-18-4	165.8		0.18	24	0.18	25	0.17	23	0.18	0.01	24	1.0
Tentatively Identified Compound^(d)													
Propane	74-98-6	44	5.5	0.26	131	0.24	120	0.21	107	0.24	0.02	120	12.0
Unknown			5.9	0.10	(g)	0.05	(g)	0.08	(g)	0.08	0.03	(h)	(h)
Methyl Alcohol	67-56-1	32	6.5	3.85	2695	3.73	2612	4.44	3107	4.01	0.38	2805	265
Butane	106-97-8	58	7.1	0.27	104	0.26	99	0.32	122	0.28	0.03	108	11.9
Methane, dichlorofluoro-	75-43-4	102	8.2	0.25	55	0.20	44	0.29	64	0.25	0.04	54.4	9.7
Ethanol	64-17-5	46	8.2	0.68	331	0.20	98	0.53	259	0.47	0.24	229	119
Butanal	123-72-8	72	13.9	0.22	68	0.24	76	0.21	64	0.22	0.02	69.2	5.8
Unknown			16.1	0.06	(g)	0.07	(g)	0.05	(g)	0.06	0.01	(h)	(h)
1-Butanol	71-36-3	74	18.0	0.40	120	0.42	128	0.36	110	0.39	0.03	119	9.1
Unknown			20.8	0.12	(g)	0.15	(g)	0.14	(g)	0.14	0.01	(h)	(h)
Unknown Alkane			24.9	0.05	(g)	0.05	(g)	0.05	(g)	0.05	0.00	(h)	(h)
Unknown			26.3	0.05	(g)	0.05	(g)	0.05	(g)	0.05	0.00	(h)	(h)

AX-102 Table D.2. (Contd)

Tentatively Identified Compound ^(a)	CAS No.	Mol Wt	Ret Time	SS-035-A04.212 ^(c)		SS-035-A05.218 ^{(e)(f)}		SS-035-A06.220 ^(g)		Mean and Standard Deviations			
				PNL 212 ^(c) (mg/m ³) (ppbv)	PNL 218 ^{(e)(f)} (mg/m ³) (ppbv)	PNL 218 ^{(e)(f)} (mg/m ³) (ppbv)	PNL 220 ^(g) (mg/m ³) (ppbv)	(mg/m ³) St Dev	(ppbv) St Dev				
4-Heptanone	123-19-3	114	29.2	0.04	7	0.05	9	0.04	8	0.04	0.00	8.2	0.9
3-Heptanone	106-35-4	114	29.8	1.10	217	1.35	265	1.05	206	1.17	0.16	229	31.1
2-Heptanone	110-43-0	114	29.9	0.04	8	0.05	10	0.03	6	0.04	0.01	7.9	1.7
Unknown			32.8	0.04	(g)	0.05	(g)	0.03	(g)	0.04	0.01	(h)	(h)
Unknown Aldehyde			33.4	0.07	(g)	0.08	(g)	0.06	(g)	0.07	0.01	(h)	(h)
Unknown			37.7	0.17	(g)	0.17	(g)	0.14	(g)	0.16	0.01	(h)	(h)

- (a) TO-14 plus 14 additional 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) Molecular weight not available for this analyte.
- (h) Mean and/or standard deviation are not meaningful for this analyte.

Table D.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single SUMMATM Canister Collected from the Headspace of Tank AX-102 on 6/27/95

Target Analytes	CAS No.	Mol Wt.	Ret Time	S5-035-A05.218 ^(c)		S5-035-A05.218 ^(c)		Relative Percent Difference %
				PNL 218 ^(d) (mg/m ³)	(ppbv)	PNL 218 ^(d) (mg/m ³)	(ppbv)	
Acetonitrile	75-05-8	41.1		0.48	262	0.53	289	9.9
Acetone	67-64-1	58.1		0.58	223	0.62	238	6.7
Trichlorofluoromethane	75-69-4	137.4		2.46	401	2.62	427	6.3
Propanenitrile	107-12-0	55.1		0.11	43	0.10	42	9.5
Propanol	71-23-8	60.1		0.06	24	0.04	15	40.0
2-Butanone	78-93-3	72.1		0.15	47	0.15	46	0.0
Butanenitrile	109-74-0	69.1		0.29	95	0.3	96	3.4
Heptane	142-82-5	100.2		0.05	12	0.06	12	18.2
Tetrachloroethylene	127-18-4	165.8		0.18	25	0.18	25	0.0
Tentatively Identified Compound^(e)								
Propane	74-98-6	44	5.5	0.24	120	0.25	127	5.8
Unknown			5.9	0.05	(f)	0.07	(f)	36.1
Methyl Alcohol	67-56-1	32	6.5	3.73	2612	4.30	3012	14.2
Butane	106-97-8	58	7.1	0.26	99	0.28	109	9.6
Methane, dichlorofluoro-	75-43-4	102	8.2	0.20	44	0.26	56	23.2
Ethanol	64-17-5	46	8.2	0.20	98	0.43	209	72.2
Butanal	123-72-8	72	13.9	0.24	76	0.22	68	9.9
Unknown			16.1	0.07	(e)	0.05	(e)	36.1
1-Butanol	71-36-3	74	18.0	0.42	128	0.43	131	2.6
Unknown			20.8	0.15	(f)	0.15	(f)	0.7
Unknown Alkane			24.9	0.05	(f)	0.05	(f)	12.5
Unknown			26.3	0.05	(f)	0.06	(f)	7.5

AX-102 Table D.3. (Contd)

Tentatively Identified Compound ^(a)	CAS No.	Mol Wt	Ret Time	S5-035-A05.218 ^(c)		S5-035-A05.218 ^(c)		Relative Percent Difference %
				PNL 218 ^(d) (mg/m ³)	(ppbv)	PNL 218 ^(d) (mg/m ³)	(ppbv)	
4-Heptanone	123-19-3	114	29.2	<0.05	<10	0.05	10	
3-Heptanone	106-35-4	114	29.8	1.35	265	1.36	268	1.3
2-Heptanone	110-43-0	114	29.9	0.05	10	0.05	10	2.0
Unknown			32.8	0.05	(f)	0.04	(f)	32.3
Unknown Aldehyde			33.4	0.08	(f)	0.09	(f)	3.6
Unknown			37.7	0.17	(f)	0.17	(f)	2.4

(a) TO-14 plus 14 additional target analytes.

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

(c) WHC sample identification number.

(d) PNL SUN/MATM 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 Ambient Air and Ambient Air Through the VSS Collected Near Tank AX-102 in SUMMATM Canisters on 8/8/95

<u>Target Analytes</u>	<u>CAS No.</u>	<u>Mol Wt</u>	<u>Ret Time</u>	<u>Ambient Air Upwind</u>	<u>Ambient Air Through VSS</u>
Acetone	67-64-1	58.08		S5-035-A01.257 ^(c) PNL 257 ^(c) (mg/m ³) (ppbv) 0.01	S5-035-A02.258 ^(c) PNL 258 ^(c) (mg/m ³) (ppbv) 0.01
				5	6

**Tentatively Identified Compound^(d).
No Compounds Identified**

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

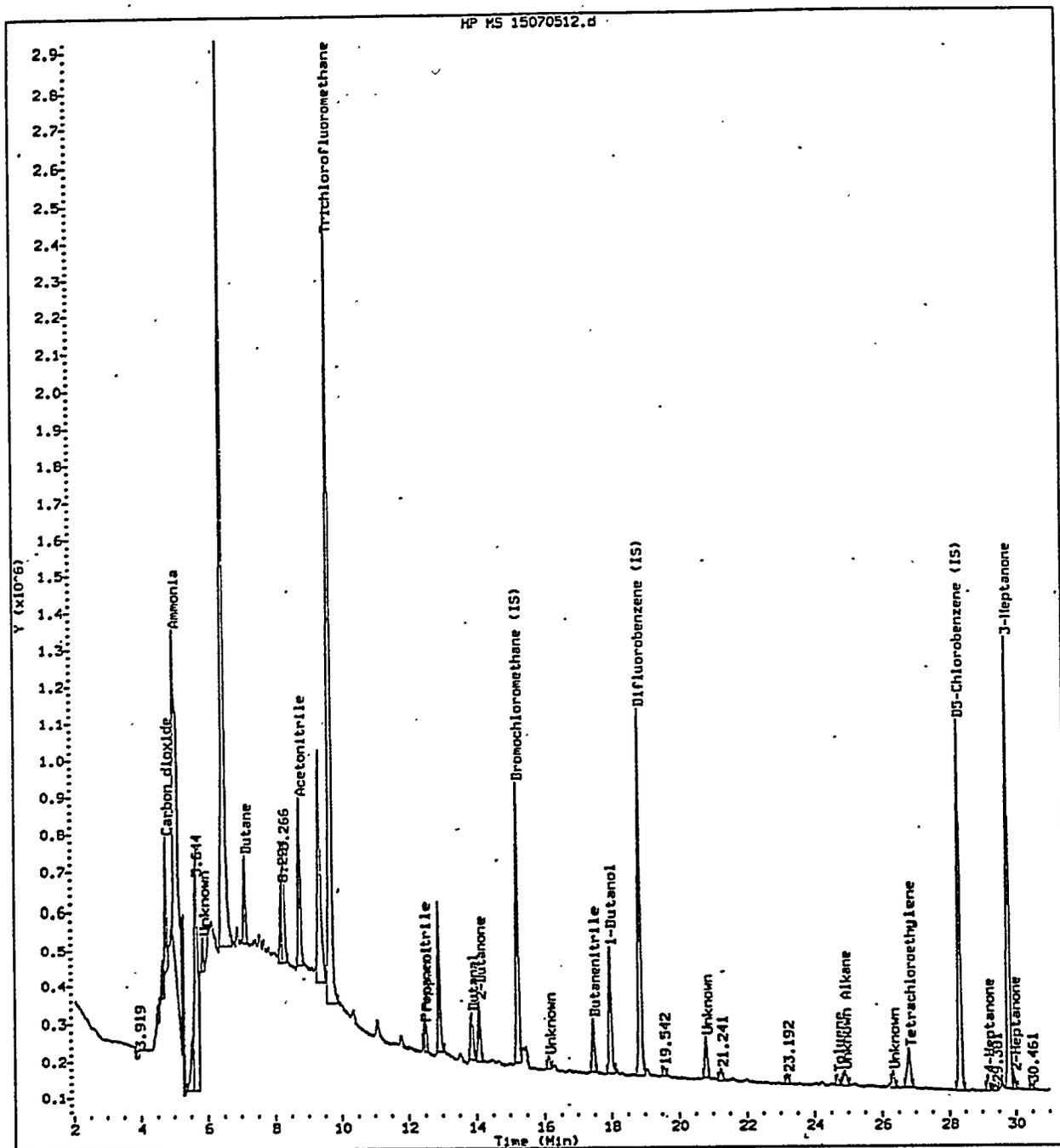


Figure D.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank AX-102
SUMMA™ Canister Sample S5035-A04-212 Collected on 6/27/95

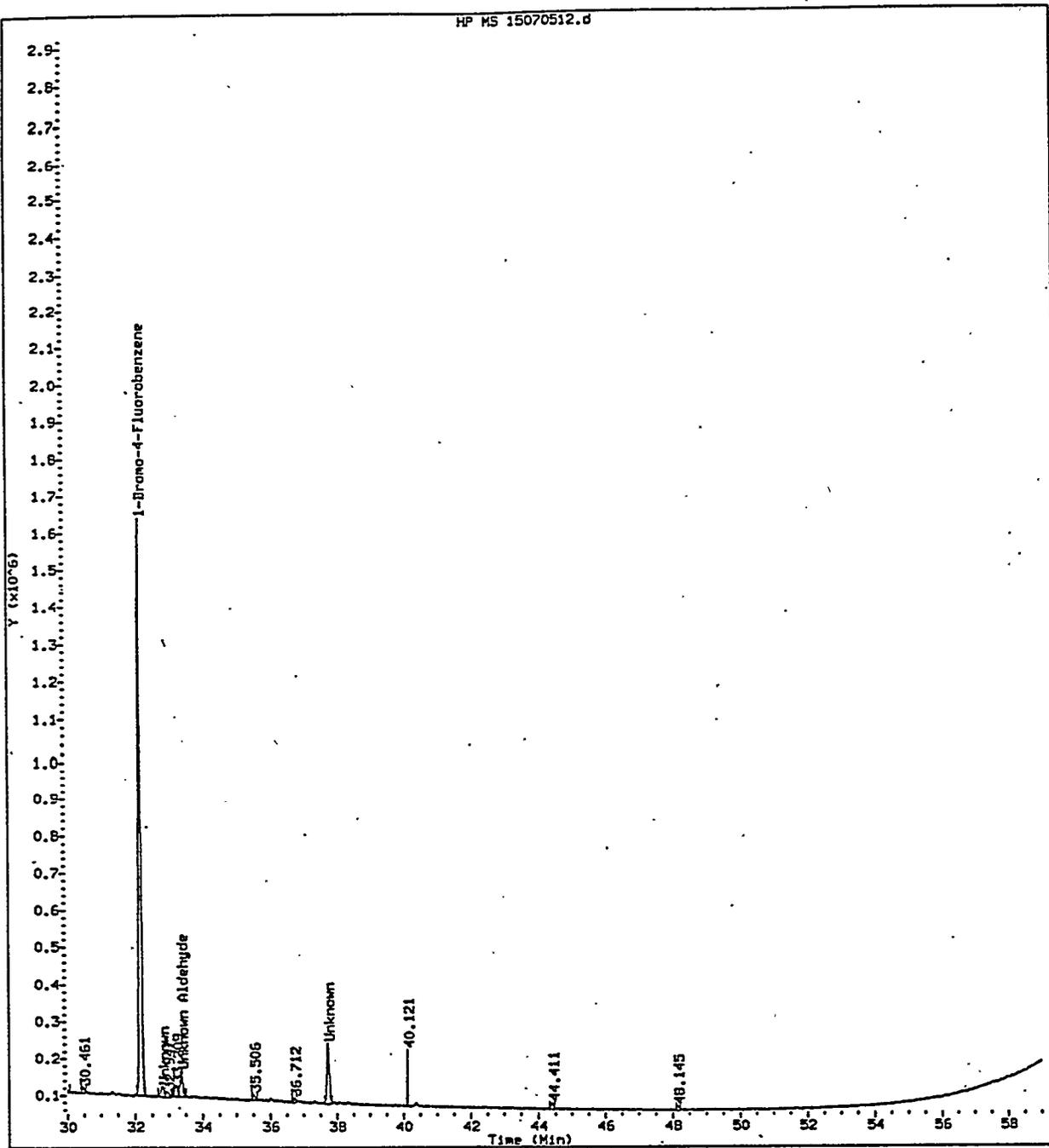


Figure D.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank AX-102
SUMMA™ Canister Sample S5035-A04-212 Collected on 6/27/95

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 TD³), which are sealed with gasketed end caps, thus providing a rugged, headspace-free shipping and storage medium. As a precautionary measure, sample tubes are kept in refrigerated storage before and after sampling.

E.2 Analytical Procedure

The Supelco 300 tubes were analyzed according to Pacific Northwest National Laboratory (PNL) Technical Procedure PNL-TVP-10^(a), with the exceptions noted in Section E.4. The method employs Supelco Carbotrap™ 300 traps for sample collection and preconcentration. The traps are ground-glass tubes (11.5 cm long X 6 mm OD, 4 mm ID) containing a series of sorbents arranged in order of increasing retentivity. Each trap contains 300 mg of Carbotrap™ C, 200 mg of Carbotrap™ B, and 125 mg of Carbosieve™ S-III. The first 2 sorbents are deactivated graphite with limited sorption power for less volatile compounds. The final trapping stage, the Carbosieve™ S-III, is a graphitized molecular sieve used to retain the most volatile components, including some permanent gases such as Freon-12. Following sample collection and addition of internal standard (IS), the traps are transferred to a Dynatherm ACEM 900 thermal desorber unit for analysis. The trap on the ACEM 900 is then desorbed by ballistic heating to 350°C with the sample then transferred to a smaller focusing trap. A 10:1 split is used during the transfer with 10% of the sample analyzed and the rest retained for reanalysis. The split sample collected on a second identical Carbotrap™ 300 trap is used for repeat analysis on at least 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 51 compounds that are directly quantified in this analysis make up the target analyte list (these 51 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table 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 met.

Table E.1 Target Organic Analytes

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

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

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

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

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

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

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

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

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

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

The IS concentrations were converted from ppbv to mg/m³ at STP using a molecular weight of 114.09 for 1,4-difluorobenzene, 117.6 for chlorobenzene-d₅, and 174.0 for 1,4 bromofluorobenzene.

E.4 Semi-Volatile Organic Sample Results

Sixteen TSTs, consisting of 12 samples, 2 field blanks, and 2 trip blanks, were returned to the laboratory on June 29, 1995, under WHC chain-of-custody 008906. The samples were analyzed on July 27, 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. Eleven target analytes above the 5-ppbv reporting cutoff and 30 TICs above the 10-ppbv reporting cutoff were detected in the tank-headspace samples. All target analytes and 29 of 30 TICs were observed in two or more sorbent traps. Ten of 29 TICs were identified as unknowns. Trichlorofluoromethane (1.54 mg/m³), acetone (0.44 mg/m³), and acetonitrile (0.29 mg/m³) accounted for 69% of the target analytes and 29% of the total concentration identified by both the target and TIC analyses. The total concentration of the target analytes was found to be 3.29 mg/m³ or 47% of the total concentration identified by both the target and TIC analyses. The predominant TICs observed in these samples were 3-heptanone (1.28 mg/m³), 1-butanol (0.52 mg/m³), and methyl alcohol (0.42 mg/m³), which accounted for 48% of the TICs and 28% of the total concentration identified by both the target and TIC analyses. The total concentration of the TICs was found to be 4.59 mg/m³ or 58% of the total concentration identified by both the target and TIC analyses. The total concentration of all the compounds identified was 7.89 mg/m³.

Triple sorbent trap sample PNL 506 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 reporting cutoff and found in both replicates. All 11 target analytes and 14 of 28 TICs had RPDs of less than 10%.

The three archived surrogates were analyzed, one of which was used to determine the response factors.

A number of problems were noted during the analysis of Tank AX-102 as noted below.

Several of the more volatile analytes, including 1,2 dichloro-1,1,2,2-tetrafluoroethane, vinyl chloride, chloroethane, and acetone, showed unacceptably large deviations from the initial calibration on the first and second calibration checks. Most of the volatile component was lost on the third calibration check. It now appears likely that the tube was damaged in preparation. The primary impact on data quality concerns acetone, which was present in the sample at high levels. The calibration for acetone is thus questionable.

Acetone and trichlorofluoromethane were detected as targets at levels above the upper calibration range for the method.

Field and trip blanks associated with Tank AX-102 showed significant anomalies that must be noted. The first trip blank showed the presence of a wide range of target compounds in a pattern

similar to but not identical with the tank samples. For example, trichlorofluoromethane was prominent in the field blank and all four tank samples. Other compounds detected in the first field blank include dichlorofluoromethane, acetonitrile, acetone, 1,1 dichloroethene, propanenitrile, 2-butanone, butanenitrile, benzene, heptane, toluene, ethylbenzene, and decane. Methyl alcohol, butanal, and 2,2 methylhexane were also detected as TICs. The second field blank was clean; however, a large air peak at the beginning of the chromatogram and low IS recoveries compromised that result. Minor traces of some target compounds were present in the first trip blank, but the second trip blank run immediately before the analysis of the tank sample was essentially clean except for traces of trichlorofluoromethane. The origin of the blank contamination in the field blank is unclear. It may be associated with contamination of the field-sampling manifold or may represent some type of handling problem with that tube. The lack of significant contamination on the two trip blanks combined with the high degree of reproducibility of the tank samples themselves for a wide range of target and TIC analytes suggests that there is no adverse effect on data quality associated with the analytical process itself, but the field sampling remains potentially questionable.

Surrogate recoveries ranged from 76 to 99% on the first and third samples, but were unacceptably low on the second sample (and repeat) ranging from 53 to 67%. Since other analytical parameters, including tank-sample analyte results, showed excellent precision, the problem appears to be related to the surrogate preparation technique by the static-dilution method, which is inherently less precise than other aspects of the TST method.

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

1. A system blank was run at the beginning of analysis as per PNL-TVP-10. The system blank was intended as an overall instrument cleanout and as such has been run without ISs. The wording of PNL-TVP-10 was inadvertently written to include ISs in the initial system blank. This was not intended and will be modified in the next revision. A system blank was not run after the samples and before the continuing calibration. A change was made subsequent to the analysis of the AX-102 run to include laboratory blanks containing ISs as spacers between standards and low-level samples of field blanks. Those will be done to absolutely verify that no analyte carryover has occurred from the continuing calibration standard. No carryover was observed in the field blanks for AX-102. Subsequent analyses using the more rigorous procedure have shown no evidence of any detectable carryover for the compounds reported here.
2. Additional surrogates, including benzene-d6, ethyl benzene-d10, and dodecane-d26, were added to the sorbent tubes before sending the tubes to the field. These compounds were used strictly for method development and were not included in the final version of PNL-TVP-10 Rev. 0.
3. Procedure PNL-TVP-10 states that four ISs are used for quantification. One of those standards, bromochloromethane, was removed from the method before any tank samples were analyzed. Bromochloromethane has been found to exhibit unacceptably erratic behavior as an IS for the TST method. The next revision of PNL-TVP-10, currently in preparation, will reflect this change.

Table E.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Triple Sorbent Traps Collected from the Headspace of Tank AX-102 on 6/27/95.

Target Analytes	CAS No.	Mol. Wt.	Ret. Time	S5035-A40.505 ^(c)		S5035-A41.506 ^{(c)(d)}		S5035-A42.507 ^(e)		Mean and Standard Deviations		
				PNL 505 ^(e) (mg/m ³) (ppbv)	PNL 506 ^(e) (mg/m ³) (ppbv)	PNL 507 ^(e) (mg/m ³) (ppbv)	(mg/m ³) StDev	(ppbv) StDev	(mg/m ³) StDev	(ppbv) StDev		
Acetonitrile	75-05-8	41.1		0.28	152	0.28	152	0.28	0.00	153	1.4	
Acetone	67-64-1	58.1		0.45	172	0.40	153	0.43	0.03	167	12.1	
Trichlorofluoromethane	75-69-4	137.4		1.53	250	1.54	251	1.54	0.01	250	0.7	
Methylene Chloride	75-09-2	84.9		0.02	6	0.03	7	0.02	0.01	6	0.7	
Propanenitrile	107-12-0	55.1		0.17	69	0.16	64	0.17	0.01	68	2.6	
Propanol	71-23-8	60.1		0.13	49	0.14	50	0.14	0.02	53	5.0	
2-Butanone	78-93-3	72.1		0.17	51	0.17	52	0.17	0.01	51	0.5	
Butanenitrile	109-74-0	69.1		0.26	86	0.26	85	0.26	0.00	85	0.7	
Heptane	142-82-5	100.2		0.06	14	0.06	14	0.06	0.00	14	0.3	
Toluene	108-88-3	92.1		0.02	5	0.02	5	0.02	0.00	6	0.4	
Tetrachloroethylene	127-18-4	165.8		0.18	25	0.19	25	0.19	0.01	25	0.5	
Tentatively Identified Compound^(b)												
Methyl Alcohol	67-56-1	32	6.7	0.40	282	0.39	271	0.48	0.05	296	34.8	
Butane	106-97-8	58	7.4	0.05	18	0.04	16	0.05	0.01	18	2.4	
Ethanol	64-17-5	46	8.5	0.12	60	0.11	55	0.11	(g)	56	(g)	
Unknown Ketone			13.9	0.04	(h)	0.05	(h)	0.06	0.01	(g)	(g)	
Butanal	123-72-8	72	14.3	0.07	21	0.12	36	0.04	0.04	22.6	12.7	
1-Butanol	71-36-3	74	18.3	0.51	155	0.53	161	0.52	0.01	158	2.8	
Unknown Aldehyde			20.0	0.05	(h)	0.06	(h)	0.04	0.01	(g)	(g)	
Propylene Glycol	57-55-6	76	21.7	0.17	51	0.13	39	0.11	0.01	49.6	1.9	
Pentanenitrile	110-59-8	83	23.7	0.05	14	0.05	14	0.08	0.02	16.4	4.5	
2-Hexanone	591-78-6	100	25.2	0.05	11	0.05	12	<0.05	(g)	11.3	(g)	
Heptane, 3-methyl-	589-81-1	114	25.5	0.08	16	0.08	15	0.08	0.00	15.5	0.6	
Unknown			26.3	0.05	(h)	0.04	(h)	0.01	0.02	(g)	(g)	
Nitric acid, butyl ester	928-45-0	119	26.9	0.07	13	0.06	10	0.06	0.01	11.4	1.4	
Butane, 1-nitro-	627-05-4	103	27.3	0.05	11	<0.05	<10	<0.05	(g)	(g)	(g)	
3-Heptanone	106-35-4	114	30.4	1.25	245	1.30	256	1.29	0.03	251.7	5.7	
3-Heptanol	589-82-2	116	31.0	0.14	26	0.13	26	0.13	0.00	25.9	0.3	
Butanamide	541-35-5	87	31.8	0.07	19	0.10	27	0.06	0.02	20.3	5.9	
Unknown			32.6	0.06	(h)	0.07	(h)	0.07	0.00	(g)	(g)	

AX-102 Table E.2 (Contd)

Tentatively Identified Compound ^(a)	CAS No.	Mol Wt	Ret Time	S5035-A40.505 ^(c)		S5035-A41.506 ^{(e)(g)}		S5035-A42.507 ^(e)		Mean and Standard Deviations		
				PNL 505 ^(e) (mg/m ³) (ppbv)	PNL 505 ^(e) (h)	PNL 506 ^(e) (mg/m ³) (ppbv)	PNL 506 ^(e) (h)	PNL 507 ^(e) (mg/m ³) (ppbv)	PNL 507 ^(e) (h)	(mg/m ³) St Dev	(ppbv) St Dev	
Unknown			33.8	0.10	(h)	0.10	(h)	0.10	(h)	0.10	0.00	(g)
Hexanal, 2-ethyl-	123-05-7	128	34.0	0.12	21	0.11	19	0.10	18	0.11	0.01	19.1
Unknown			34.5	0.07	(h)	0.01	(h)	0.01	(h)	0.03	0.03	(g)
Unknown			35.0	0.05	(h)	0.04	(h)	0.03	(h)	0.04	0.01	(g)
Unknown			36.2	0.20	(h)	0.18	(h)	0.17	(h)	0.18	0.02	(g)
1-Hexanol, 2-ethyl-	104-76-7	130	37.3	0.14	25	0.14	24	0.13	22	0.14	0.01	23.6
Unknown Alcohol			38.4	0.18	(h)	0.17	(h)	0.18	(h)	0.18	0.00	(g)
Unknown Ketone			43.9	0.07	(h)	0.08	(h)	0.07	(h)	0.07	0.00	(g)
Dodecane	112-40-3	170	45.1	0.08	11	0.09	11	0.09	11	0.08	0.00	11.1
Tridecane	629-50-5	184	48.8	0.21	26	0.22	26	0.22	27	0.22	0.00	26.3
Tetradecane	629-59-4	198	52.3	0.09	10	0.09	10	0.09	10	0.09	0.00	10.3

(a) TO-14 plus 14 additional 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.

(h) Molecular weight not available

**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 AX-102 on 6/27/95**

Target Analytes	CAS No.	Mol Wt	S5035-A41.506 ^(c)		S5035-A41.506 ^(c)		Relative Percent Difference %
			PNL 506 ^(c) (mg/m ³) (ppbv)	PNL 506 ^(c) (ppbv)	PNL 506 ^(c) (mg/m ³) (ppbv)	PNL 506 ^(c) (ppbv)	
Acetonitrile	75-05-8	41.1	0.28	152	0.26	143	6.3
Acetone	67-64-1	58.1	0.40	153	0.40	153	0.3
Trichlorofluoromethane	75-69-4	137.4	1.54	251	1.44	235	6.7
Methylene Chloride	75-09-2	84.9	0.03	7	0.03	7	0.0
Propanenitrile	107-12-0	55.1	0.16	64	0.15	63	2.6
Propanol	71-23-8	60.1	0.14	50	0.13	48	7.4
2-Butanone	78-93-3	72.1	0.17	52	0.16	51	6.1
Butanenitrile	109-74-0	69.1	0.26	85	0.26	85	0.0
Heptane	142-82-5	100.2	0.06	14	0.06	15	0.0
Toluene	108-88-3	92.1	0.02	5	0.02	5	0.0
Tetrachloroethylene	127-18-4	165.8	0.19	25	0.19	25	0.0
Tentatively Identified Compound^(a)							
Methyl Alcohol	67-56-1	32	0.39	271	0.27	188	36.3
Butane	106-97-8	58	0.04	16	0.10	40	84.9
Ethanol	64-17-5	46	0.11	55	0.06	27	67.5
Unknown Ketone			0.05	(f)	0.04	(f)	13.6
Butanal	123-72-8	72	0.12	36	0.06	17	69.8
Unknown Aldehyde			0.06	(f)	0.02	(f)	82.9
Propylene Glycol	57-55-6	76	0.13	39	0.15	43	10.8
Pentanenitrile	110-59-8	83	0.05	14	0.06	16	17.9
2-Hexanone	591-78-6	100	0.05	12	0.05	11	9.7
Heptane, 3-methyl-	589-81-1	114	0.08	15	0.08	16	6.3
Unknown			0.04	(f)	0.04	(f)	15.4
Nitric acid, butyl ester	928-45-0	119	0.06	10	0.05	10	1.8
Butane, 1-nitro-	627-05-4	103	<0.05	<10	<0.05	<10	
3-Heptanone	106-35-4	114	1.30	256	1.29	253	1.2
3-Heptanol	589-82-2	116	0.13	26	0.13	26	0.7
Butanamide	541-35-5	87	0.10	27	0.07	17	43.3
Unknown			0.07	(f)	0.07	(f)	1.4
Unknown			0.10	(f)	0.09	(f)	3.2
Hexanal, 2-ethyl-	123-05-7	128	0.11	19	0.09	16	12.0
Unknown			0.01	(f)	0.02	(f)	53.3

AX-102 Table E.3. (Contd)

Tentatively Identified Compound ^(a)	CAS No.	Mol Wt	S5035-A41.506 ^(c)		S5035-A41.506 ^(c)		Relative Percent Difference %
			PNL 506 ^(c) (mg/m ³)	(ppbv)	PNL 506 ^(c) (mg/m ³)	(ppbv)	
Unknown			35.0	(f)	0.03	(f)	29.4
Unknown			36.2	(f)	0.18	(f)	2.8
1-Hexanol, 2-ethyl-	104-76-7	130	37.3	24	0.14	23	4.3
Unknown Alcohol			38.4	(f)	0.17	(f)	4.7
Unknown Ketone			43.9	(f)	0.07	(f)	2.7
Dodecane	112-40-3	170	45.1	11	0.09	11	0.0
Tridecane	629-50-5	184	48.8	26	0.22	26	0.0
Tetradecane	629-59-4	198	52.3	10	<0.09	<10	

(a) TO-14 plus 14 additional target analytes.

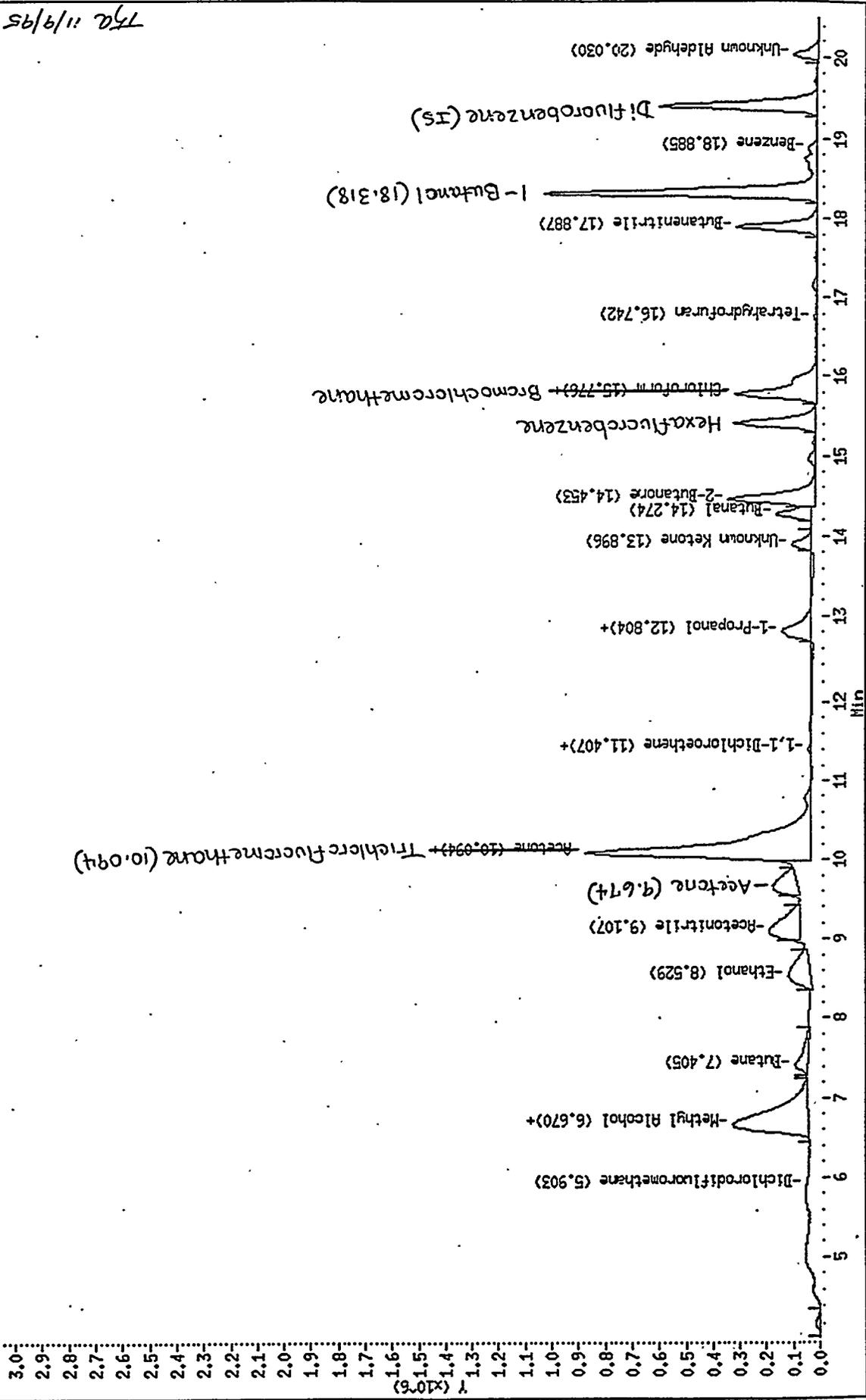
(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.

(c) WHC sample identification number.

(d) PNL sample number.

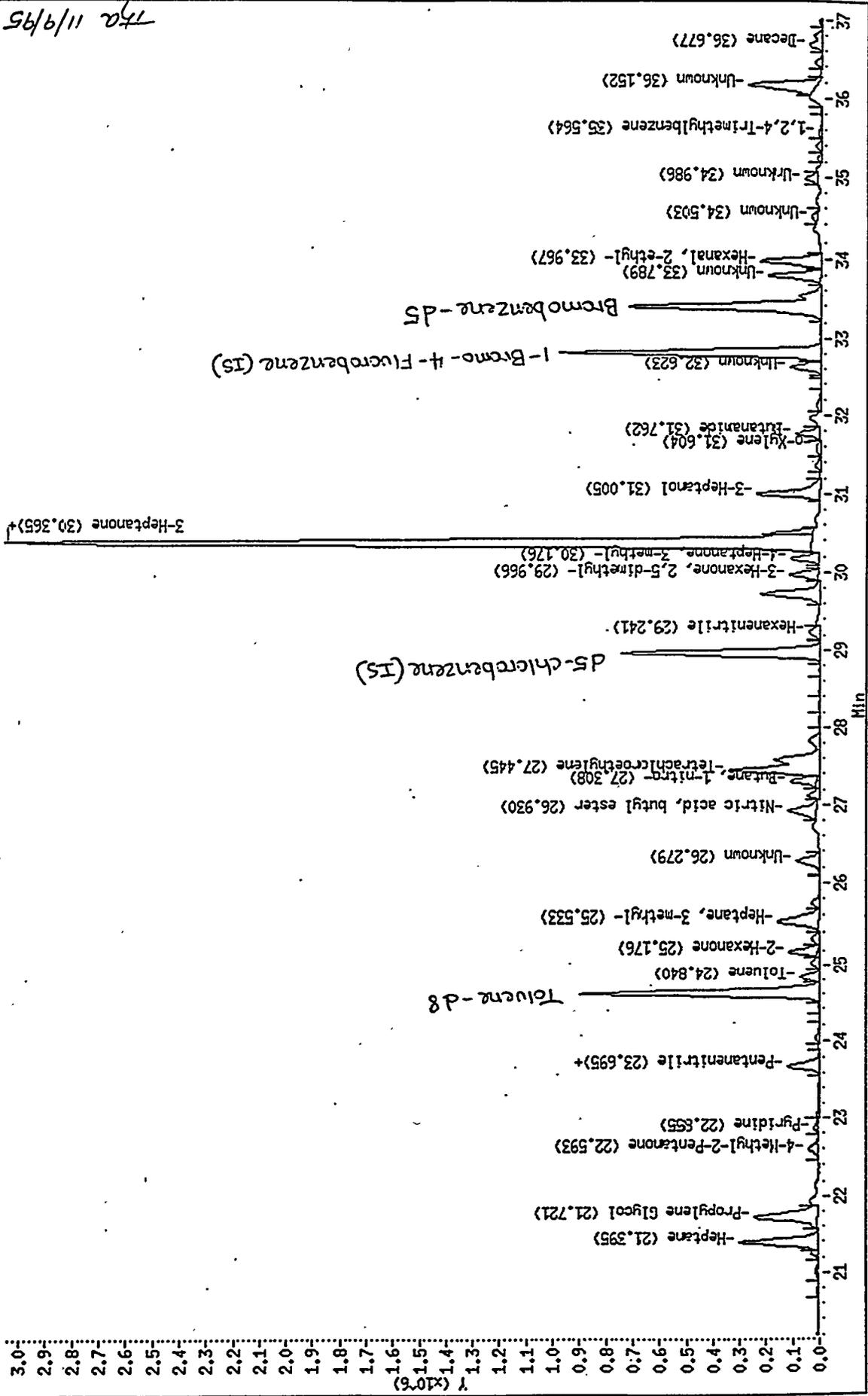
(e) Obtained by mass spectral interpretation and comparison with the EPA/NIST/WILEY Library.

(f) No molecular weight available for calculation.



TJA 11/9/95

Figure E.1a Total Ion Chromatogram (0 - 20 min) for Hanford Waste Tank AX-102 Triple Sorbent Trap
Sample S5035-A40-505 Collected on 6/27/95



75a 11/9/95

Figure E.1b Total Ion Chromatogram (21 - 37 min) for Hanford Waste Tank AX-102 Triple Sorbent Trap Sample S5035-A40-505 Collected on 6/27/95

7/2 11/9/95

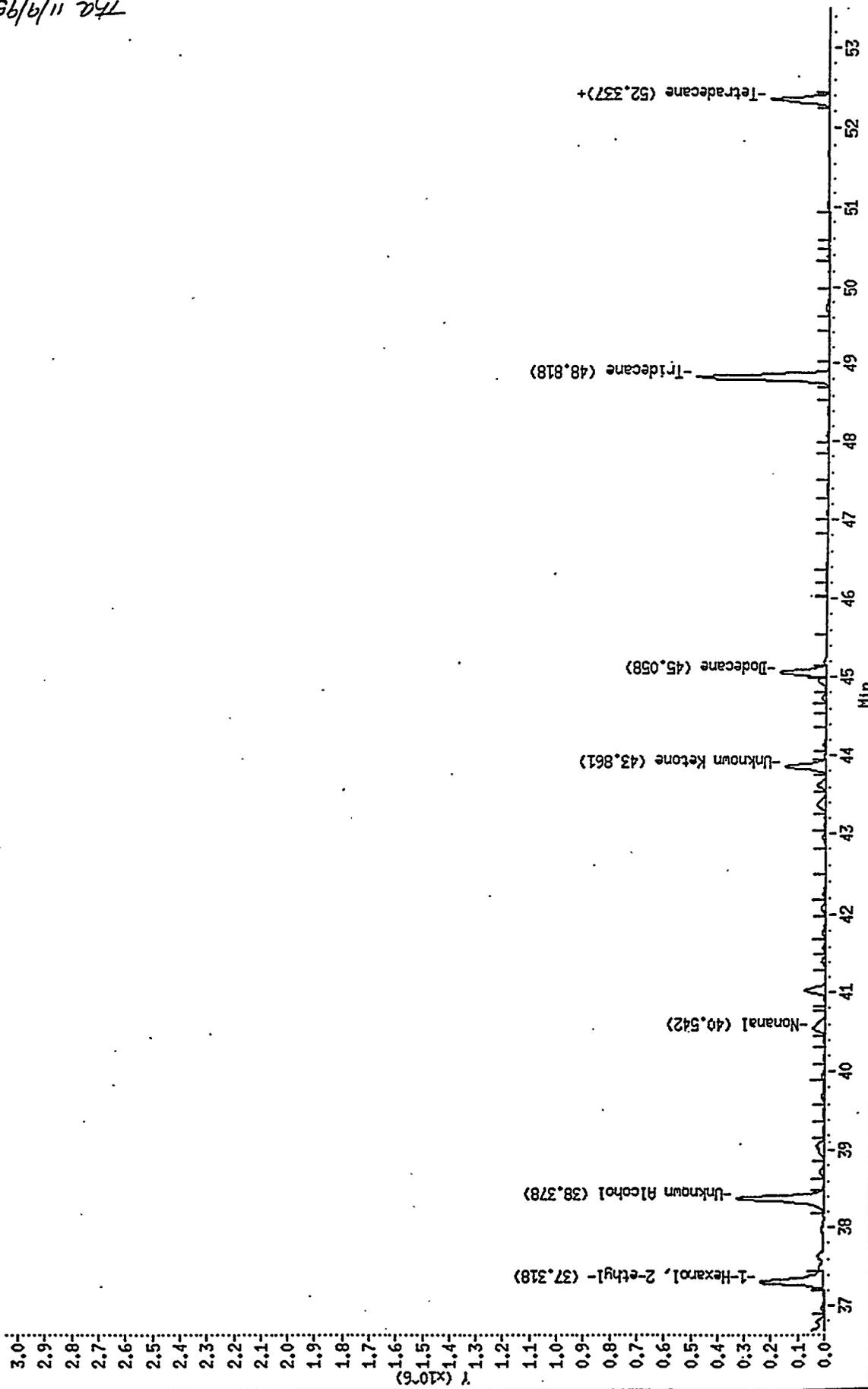


Figure E.1c Total Ion Chromatogram (37 - 53 min) for Hanford Waste Tank AX-102 Triple Sorbent Trap Sample S5035-A40-505 Collected on 6/27/95

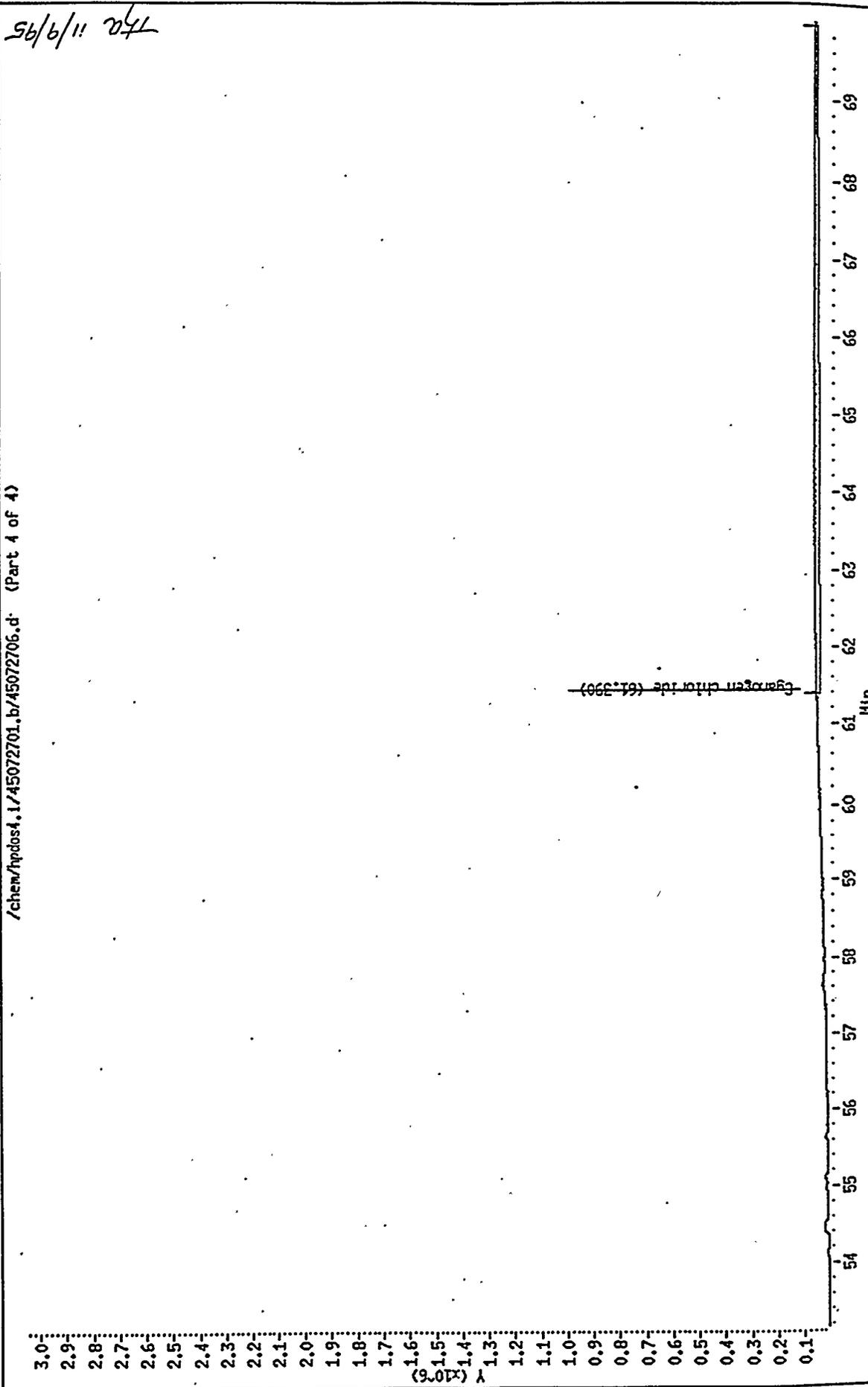


Figure E.1d Total Ion Chromatogram (54 -69 min) for Hanford Waste Tank AX-102 Triple Sorbent Trap
Sample S5035-A40-505 Collected on 6/27/95

Appendix F

Tank Vapor Characterization: Chain-of-Custody Sample Control Forms

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-AX-102 Tank Vapor Sample SAF S5-035
(VSS Truck)

Collection date 06-27-95
Preparation date 05-26-95

Ice Chest No.

Field Logbook No. WHC-N-447-10

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

S5-035 - A23 . U36 .	NH ₃ /NO _x /H ₂ O (Sorbent Trap # 1)	Line # 9
S5-035 - A24 . U37 .	NH ₃ /NO _x /H ₂ O (Sorbent Trap # 2)	Line # 10
S5-035 - A25 . U38 .	NH ₃ /NO _x /H ₂ O (Sorbent Trap # 3)	Line # 8
S5-035 - A26 . U39 .	NH ₃ /NO _x /H ₂ O (Sorbent Trap # 4)	Line # 10
S5-035 - A27 . U40 .	NH ₃ /NO _x /H ₂ O (Sorbent Trap # 5)	Line # 9
S5-035 - A28 . U41 .	NH ₃ /NO _x /H ₂ O (Sorbent Trap # 6)	Line # 10
S5-035 - A29 . U42 .	NH ₃ /NO _x /H ₂ O (Trap Trip Blank # 1)	
S5-035 - A30 . U43 .	NH ₃ /NO _x /H ₂ O (Trap Trip Blank # 2)	
S5-035 - A31 . U44 .	NH ₃ /NO _x /H ₂ O (Trap Trip Blank # 3)	
S5-035 - A32 . U45 .	NH ₃ /NO _x /H ₂ O (Trap Field Blank # 1)	Line # 8
S5-035 - A33 . U46 .	NH ₃ /NO _x /H ₂ O (Trap Field Blank # 2)	Line # 9
S5-035 - A34 . U47 .	NH ₃ /NO _x /H ₂ O (Trap Field Blank # 3)	Line # 10

[] Field Transfer of Custody		[] Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
G W Dennis <i>J.W.D.</i>	05-30-95	0930	J A Edwards <i>J Edwards</i>	05-30-95	0930	
J A Edwards <i>J A Edwards</i>	05-31-95	0900	T B Utecht <i>T B Utecht</i>	05-31-95	0900	
<i>T B Utecht / T B Utecht</i>	6-29-95	1415	J A Edwards / J A Edwards	06-29-95	1415	
J A Edwards <i>J A Edwards</i>	7-5-95	0945	G.W. Dennis <i>G.W. Dennis</i>	7-5-95	0945	
G W Dennis <i>G.W. Dennis</i>	7-11-95	1210	K.H. Pool <i>K.H. Pool</i>	7-11-95	1210	

Final Sample Disposition

Comments:

PNL (only) Checklist	Pick-up / Delivery	Comments:
Media labeled and checked?	<input checked="" type="checkbox"/> Y / <input type="checkbox"/> N	
Letter of instruction?	<input checked="" type="checkbox"/> Y / <input type="checkbox"/> N	
Media in good condition?	<input checked="" type="checkbox"/> Y / <input type="checkbox"/> N	
COC info/signatures complete?	<input checked="" type="checkbox"/> Y / <input type="checkbox"/> N	
Sorbents shipped on ice? (<10°C)	<input checked="" type="checkbox"/> Y / <input type="checkbox"/> N	
Rad release stickers on samples?	<input checked="" type="checkbox"/> Y / <input type="checkbox"/> N	
Activity report from 2225?	<input checked="" type="checkbox"/> Y / <input type="checkbox"/> N	
COC copy for LRB, RIDS filed?	<input checked="" type="checkbox"/> Y / <input type="checkbox"/> N	
COC copy for sorbent follow-on?	<input checked="" type="checkbox"/> Y / <input type="checkbox"/> N	Original COC follows sorbent media
	POC <input checked="" type="checkbox"/> <input type="checkbox"/>	

(Revised 05/10/95 PNL)

Only Form Initiator J. A. Edwards - PNL
 Company Contact R. D. Mahon - WHC
 Project Designation/Sampling Locations 200 West Tank Farm
 241-AX-102 Tank Vapor Sample SAF S5-035
 (VSS Truck)
 Ice Chest No.
 Bill of Lading/Airbill No. N/A
 Method of Shipment Government Truck
 Shipped to PNL
 Possible Sample Hazards/Remarks Unknown at time of sampling

Telephone (509) 373-0141
 Page 85-3009 / FAX 376-0418
 Telephone (509) 373-2891
 Page 85-3152 / FAX 373-3793
 Collection date 06 - 27 - 95
 Preparation date 05 - 26 - 95
 Field Logbook No. WHC-N-642-10
 Offsite Property No. N/A

Sample Identification

S5-035 - A01 . 257
 S5-035 - A02 . 258

Ambient Air SUMMA #1 Upwind of AX-102
 Ambient Air SUMMA #2 Through Port 15

S5-035 - A04 . 212
 S5-035 - A05 . 218
 S5-035 - A06 . 220

SUMMA #3 Port 11
 SUMMA #4 Port 13
 SUMMA #5 Port 15

Field Transfer of Custody		Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
J A Edwards	05-31-95	0900	T B Utecht	05-31-95	0900	
T B Utecht	06-27-95	1415	J A EDWARDS	06-27-95	1415	

Final Sample Disposition

Comments:

PNL (only) Checklist	Pick-up / Delivery	Comments:
0 Media labeled and checked?	0 N	
0 Letter of instruction?	0 N	
0 Media in good condition?	0 N / 0 N	
0 COC info/signatures complete?	0 N / 0 N	
0 Rad release stickers on samples?	0 N / 0 N	
0 Activity report from 2225?	0 N / 0 N	
0 COC copy for LRB, RIDS filed?	0 N / 0 N	

POC JE POC JE

(Revised 10/17/94 PNL)

Only 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-AX-102 Tank Vapor Sample SAF S5-035 (VSS Truck)
 Collection date: 06-27-95
 Preparation date: 06-21-95
 Field Logbook No. WHC-H-697-10
 Ice Chest No.:
 Erico Hi/Lo thermometer No.: PNL-T-001
 Bill of Lading/Airbill No.: N/A
 Method of Shipment: Government Truck
 Shipped to: WHC
 Possible Sample Hazards/Remarks: Unknown at time of sampling
 Offsite Property No.: N/A

Sample Identification

S5-035 - A35 . 500 .	Collect PNL Triple Sorbent Trap (TST) Sample # 1	Line # <u>2</u>
S5-035 - A36 . 501 .	PNL TST Sample # 2	Line # <u>4</u>
S5-035 - A37 . 502 .	PNL TST Sample # 3	Line # <u>6</u>
S5-035 - A38 . 503 .	Open, close & store PNL TST Field Blank # 1	In VSS truck
S5-035 - A39 . 504 .	PNL TST Sample # 4	Line # <u>8</u>
S5-035 - A40 . 505 .	PNL TST Sample # 5	Line # <u>2</u>
S5-035 - A41 . 506 .	PNL TST Sample # 6	Line # <u>4</u>
S5-035 - A42 . 507 .	PNL TST Sample # 7	Line # <u>6</u>
S5-035 - A43 . 508 .	PNL TST Sample # 8	Line # <u>2</u>
S5-035 - A44 . 509 .	PNL TST Sample # 9	Line # <u>2</u>
S5-035 - A45 . 510 .	Open, close & store PNL TST Field Blank # 2	In VSS truck
S5-035 - A46 . 511 .	PNL TST Sample # 10	Line # <u>4</u>
S5-035 - A47 . 512 .	PNL TST Sample # 11	Line # <u>6</u>
S5-035 - A48 . 513 .	PNL TST Sample # 12	Line # <u>8</u>
S5-035 - A49 . 514 .	Store PNL TST Trip Blank # 1	None
S5-035 - A50 . 515 .	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	06-26-95	1030	Tim Utecht	06-26-95	1030
T.B. Utecht	06-29-95	1415	J.A. Edwards	06-29-95	1415

Final Sample Disposition

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

Comments:
 Cooler Temperature Status
 III 7 °C/Lo 5 °C (pick up at PNL to WHC) |
 III 7 °C/Lo 5 °C (delivery at WHC from PNL) |
 III 6 °C/Lo 5 °C (at return to PNL from WHC) |
 III 7 °C/Lo 5 °C (at delivery from WHC to PNL) |

(Revised 06/21/95 PNL)

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