

TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank 241-U-109: Results from Samples Collected on 8/10/95

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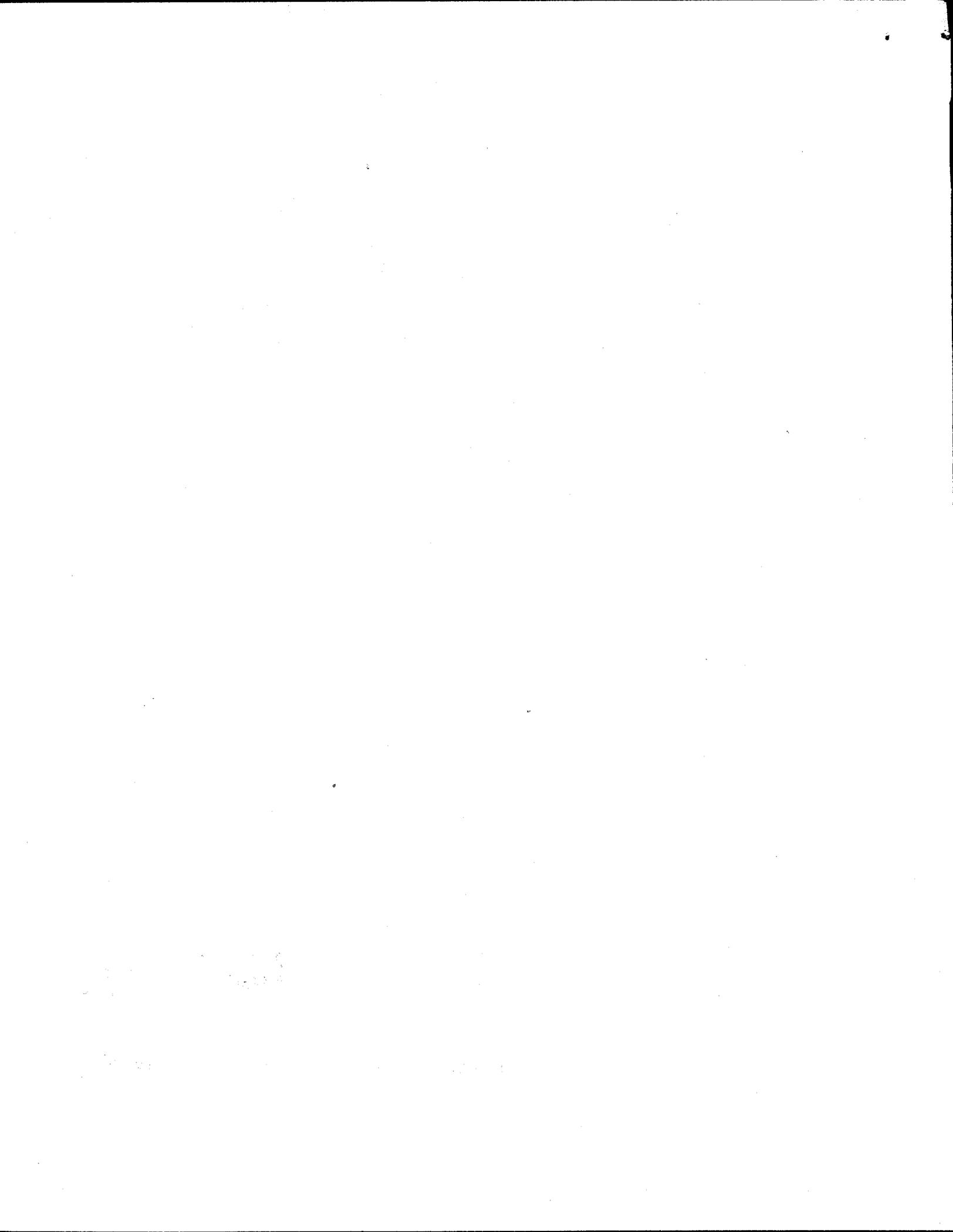
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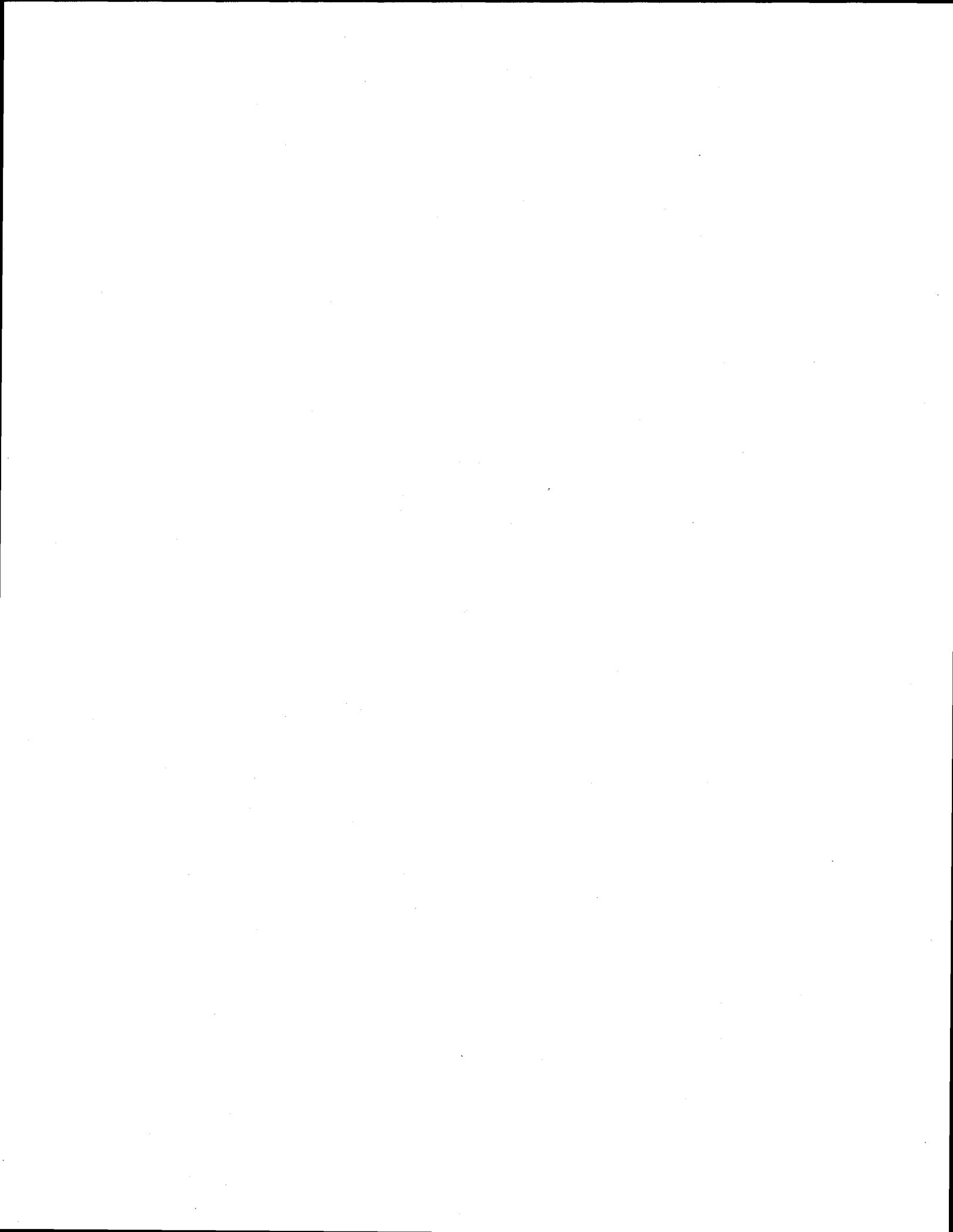
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Summary

This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-U-109 (Tank U-109) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support safety evaluations and tank farm operations. The results include air concentrations of selected inorganic and organic analytes and grouped compounds from samples obtained by Westinghouse Hanford Company (WHC) and provided for analysis to Pacific Northwest National Laboratory (PNNL). Analyses were performed by the Vapor Analytical Laboratory (VAL) at PNNL. Analyte concentrations were based on analytical results and, where appropriate, sample volumes provided by WHC. A summary of the inorganic analytes, permanent gases, and total non-methane hydrocarbons is listed in Table S.1. The three highest concentration analytes detected in SUMMA™ canister and triple sorbent trap samples is also listed in Table S.1. Detailed descriptions of the analytical results appear in the text.

Table S.1 Summary Results of Samples to Characterize the Headspace of Tank U-109 on 08/10/95.

<u>Category</u>	<u>Sample Medium</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic Analytes ^(b)	Sorbent Traps	NH ₃	577 ± 20	ppmv
		NO ₂	≤ 0.06	ppmv
		NO	≤ 0.06	ppmv
		H ₂ O	14.8 ± 0.4	mg/L
Permanent Gases	SUMMA™ Canister	CO ₂	<25	ppmv
		CO	<25	ppmv
		CH ₄	<25	ppmv
		H ₂	748	ppmv
		N ₂ O	868	ppmv
Total Non-Methane Hydrocarbons (TO-12)	SUMMA™ Canister	Hydrocarbons	9.25	mg/m ³
Volatile Organics (TO-14)	SUMMA™ Canister	Methyl Alcohol	0.408	ppmv
		Trichlorofluoromethane	0.350	ppmv
		Acetone	0.223	ppmv
Semi-Volatile Organics (PNL-TVP-10)	Sorbent Traps	Ethane, 1-chloro-1,1-difluoro-	0.733	ppmv
		Ethanol	0.432	ppmv
		Trichlorofluoromethane	0.330	ppmv

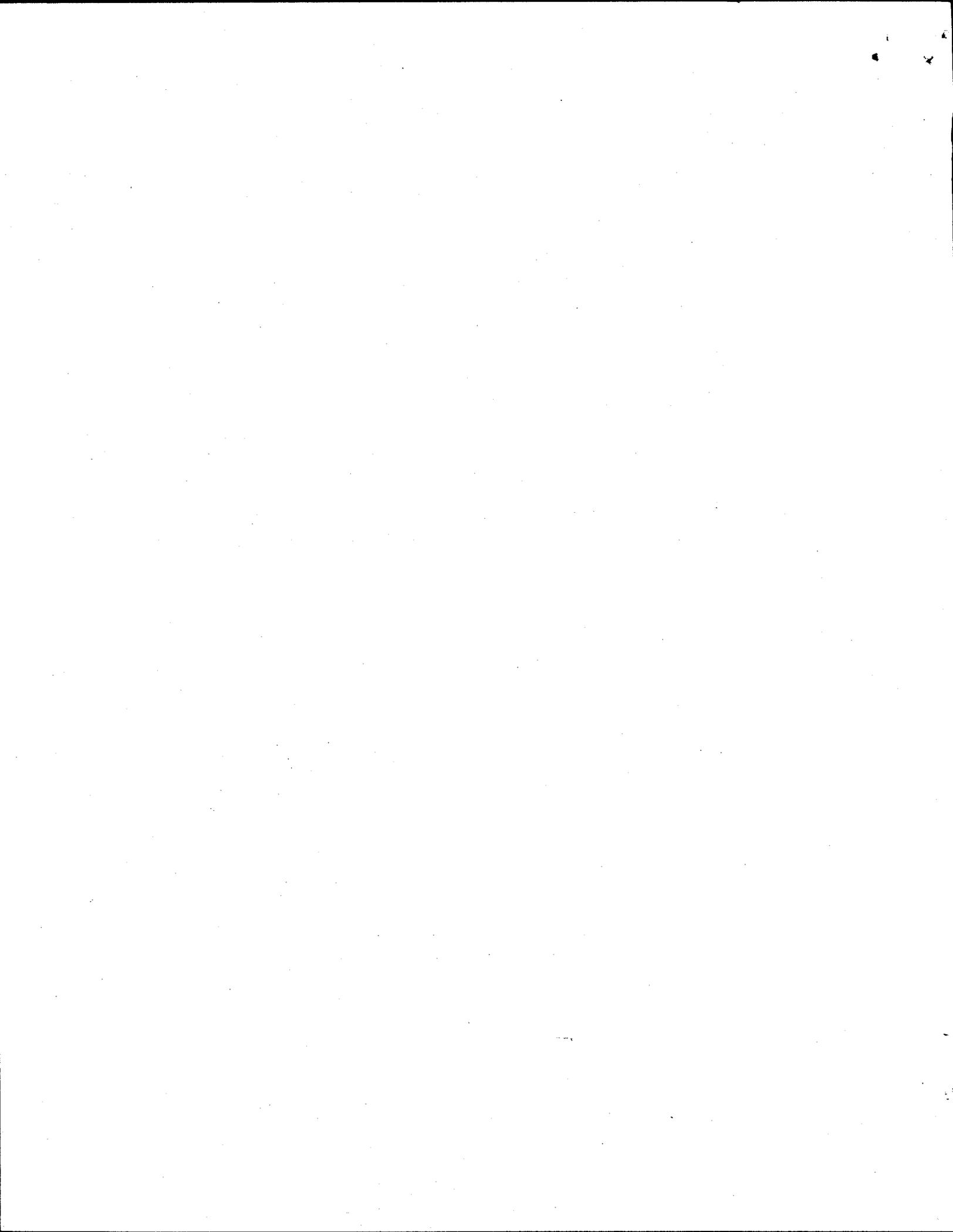
(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data.

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



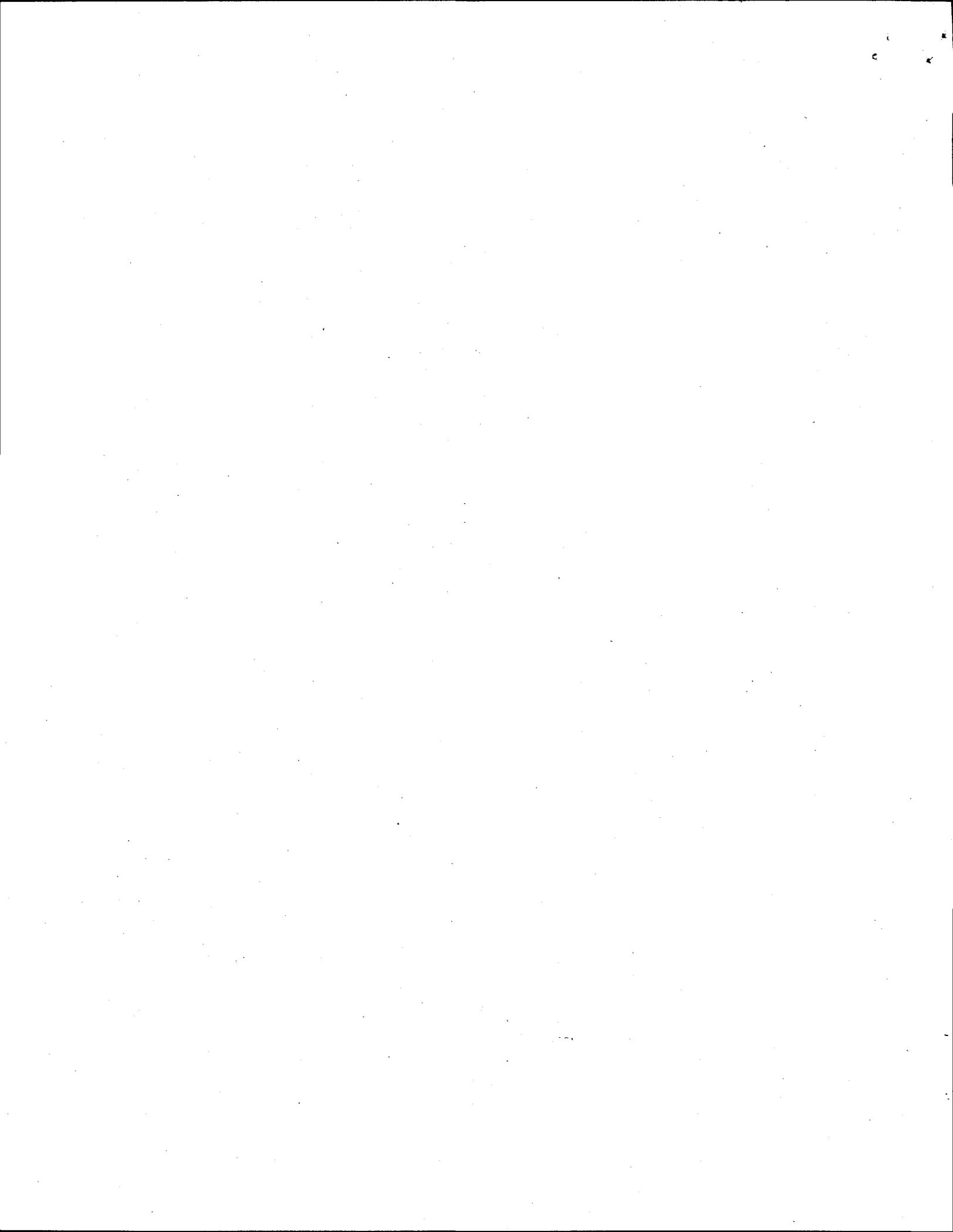
Acknowledgments

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Glossary

CAS	Chemical Abstracts Service
CCV	continuing calibration verification
COC	chain-of-custody
C _v	concentration by volume
DIW	deionized water
EPA	U.S. Environmental Protection Agency
GC/FID	gas chromatography/flame ionization detector
GC/MS	gas chromatograph/mass spectrometer
GC/TCD	gas chromatography/thermal conductivity detection
IC	ion chromatography
IL	impact level
IS	internal standard
MDL	method detection limit
NIST	National Institute for Standards and Technology
PNL	previous designation for Pacific Northwest Laboratory
PNNL	Pacific Northwest National Laboratory
ppbv	part per billion by volume
ppm	parts per million
ppmv	part per million by volume
QA	quality assurance
RPD	relative percent difference
RSD	relative standard deviation
SAP	sample and analysis plan
SCIC	suppressed-conductivity ion chromatography
SRM	standard reference material
STP	standard temperature and pressure
SUMMA™	stainless steel, passivated interior canister
TEA	triethanolamine
TIC	tentatively identified compound
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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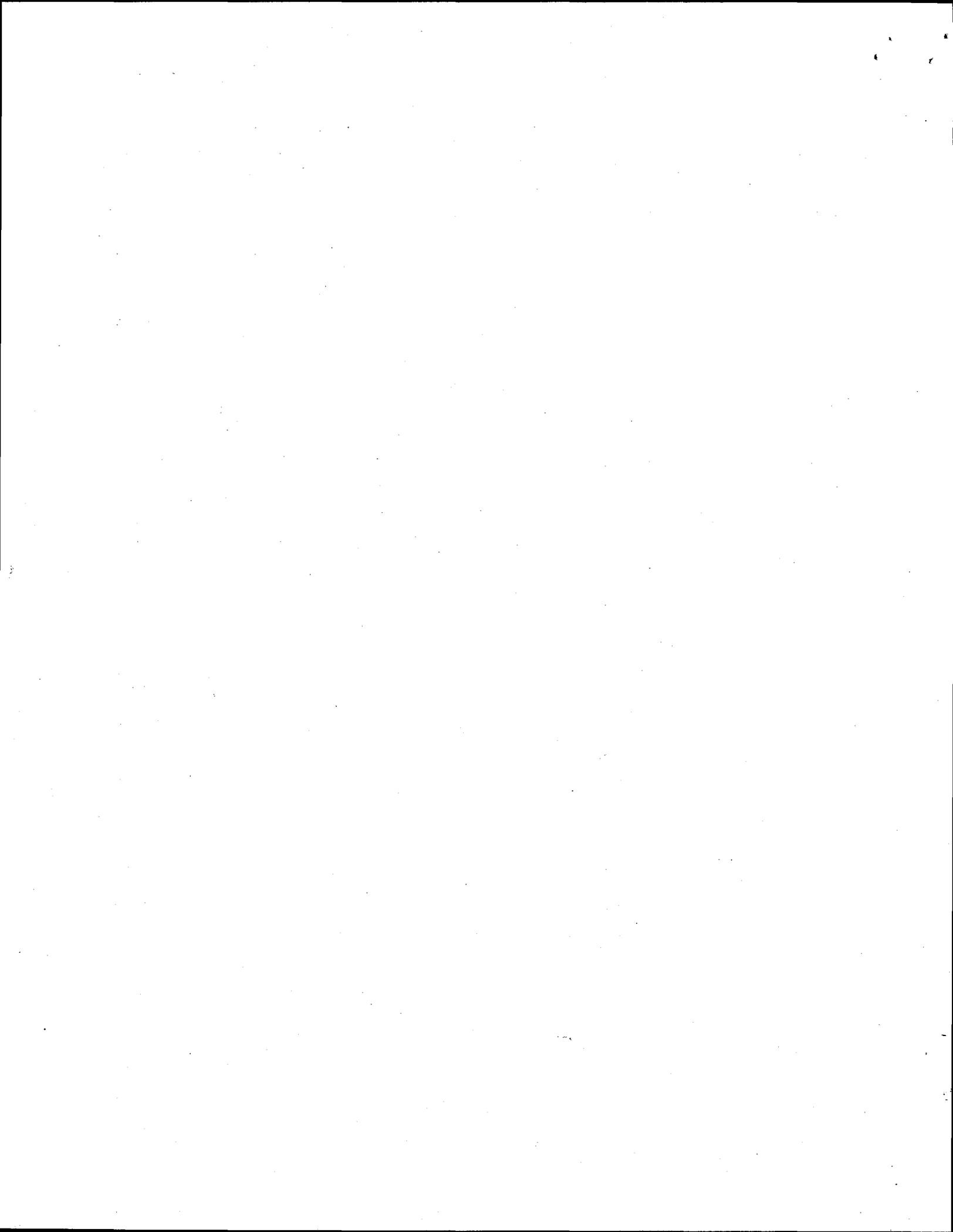
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1.0 Introduction

This report describes the results of vapor samples taken from the headspace of waste storage tank 241-U-109 (Tank U-109) at the Hanford. Pacific Northwest National Laboratory (PNNL)^(a) contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and analyze samples for inorganic and organic analytes collected from the tank headspace and ambient air near the tank. The analytical work was performed by the PNNL Vapor Analytical Laboratory (VAL) by the Tank Vapor Characterization Project. Work performed was based on a sample and analysis plan (SAP) prepared by WHC. The SAP provided job-specific instructions for samples, analyses, and reporting. The SAP for this sample job was "Vapor Sampling and Analysis Plan" (Homi 1995), and the sample job was designated S5055. Samples were collected by WHC on August 10, 1995 using the Vapor Sampling System (VSS), a truck-based sampling method using a heated probe inserted into the tank headspace.

Sampling devices and controls provided for this job included 11 sorbent trains for selected inorganic analytes (eight sample trains and three field blanks), 5 SUMMA™ canisters for permanent gases and volatile organic analytes (three samples and two ambient canisters), and 10 triple-sorbent traps (TSTs) for semi-volatile organic analytes (six samples, two field blanks, and two trip blanks). The samples and controls were provided to WHC on August 9, 1995. Exposed samples and controls were returned to PNNL on August 14, 1995. Samples and controls were handled, stored, and transported using chain-of-custody (COC) forms to ensure sample quality was maintained.

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

Tank headspace samples were analyzed for

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

-
- (a) Pacific Northwest National Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. The previous name for the laboratory was Pacific Northwest Laboratory (PNL). The former name is used when previously published documents are referenced.
- (b) PNL-TVP-07, Rev. 0, October 1994, *Sample Shipping and Receiving Procedure for PNL Waste Tank Samples*, PNL Technical Procedure, Tank Vapor Project, Richland, Washington.

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

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

2.0 Analytical Results

Samples obtained by WHC from the headspace of Tank U-109 on 8/10/95 (Sample Job S5055) were analyzed in the PNNL Vapor Analytical Laboratory. Summarized results are described in this section; details of samples, analyses, and data tables are provided in the attached appendices.

2.1 Inorganic Analytes

The vapor concentrations of selected inorganic analytes NH_3 , NO_2 , NO and vapor mass concentration (primarily H_2O), were determined. The average and one standard deviation of concentration results from inorganic sorbent sample trains used to sample headspace vapors were 577 ± 20 ppmv (NH_3), ≤ 0.06 ppmv (NO_2), ≤ 0.06 ppmv (NO), and 14.8 ± 0.4 mg/L (primarily H_2O). The vapor concentration results were based on six samples for each compound (eight samples for mass concentration). The NO_2 and NO samples included four samples trailing (downstream of) NH_3 sorbent traps and two samples unprotected by NH_3 sorbent traps. All samples (100%) were successfully analyzed and used in the averages. Representative field blanks were also analyzed and used to correct data.

Two of the four average concentration results exceeded the minimum of the expected ranges: NH_3 and H_2O . The precision of results, based on one standard deviation of all samples, was $\pm 4\%$ (within the target level of $\pm 25\%$) for analytes exceeding expected levels. 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. These uncertainties were confirmed by evaluation of spikes and continuing calibration standards (NH_3) and evaluation of the variability of field blanks (H_2O). No procedural deviations were noted. Data and additional information on samples, analyses, and results are described in Appendix A. The chain-of-custody form used to control samples, 009253, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent gas analysis of Tank U-109 can be found in Appendix B of this report. In summary, hydrogen (748 ppmv) and nitrous oxide (868 ppmv) were observed above the method detection limit (MDL) in the tank headspace samples, and carbon dioxide in the headspace samples was at a lower concentration than observed in the ambient air.

2.3 Total Non-Methane Hydrocarbons

The complete results of the TO-12 analysis of Tank U-109 can be found in Appendix C of this report. In summary, the average concentration in the three tank headspace samples was 9.25 mg/m^3 . This compares to 6.49 mg/m^3 for the sum of all compounds identified in the target and tentatively identified compound (TIC) analysis of the SUMMA™ canisters.

2.4 Volatile Organic Analytes

The complete results of the TO-14 analysis of Tank U-109 can be found in Appendix D of this report. In summary, 17 target analytes above the 5-ppbv reporting cutoff and 12 TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. All target analytes and 11 of 12 TICs were identified in two or more tank headspace samples. The total concentration of the target analytes was found to be 4.65 mg/m³. The total TIC concentration was found to be 1.84 mg/m³. The total concentration of all the compounds identified was 6.49 mg/m³. SUMMA™ canister PNL 254 was analyzed in replicate for target analytes and TICs to determine analytical precision. Fifteen of 17 target analytes and 9 of 10 TICs had relative percent differences (RPDs) of less than 10%. Pyridine and 2-butanone were the only target analytes observed in the ambient-air samples. No target analytes were observed in 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 U-109 can be found in Appendix E of this report. In summary, 20 target analytes above the 5-ppbv reporting cutoff and 11 TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. Nineteen of 20 target analytes and 9 of 11 TICs were observed in two or more sorbent traps. Two of 11 TICs were identified as unknowns. The total concentration of the target analytes was found to be 6.07 mg/m³. The total concentration of the TICs was found to be 4.84 mg/m³. The total concentration of all the compounds identified was 10.91 mg/m³. Triple sorbent trap sample PNL 649 was analyzed in replicate for target analytes and TICs to determine analytical precision. Seventeen of 20 target analytes and 4 of 9 TICs had RPDs of less than 10%. 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 17 target analytes and 2 TICs that were common to both analyses. Seventeen of 19 compounds were higher in the TST than the SUMMA™ samples. In addition, five compounds were observed in the SUMMA™ samples but not in the TST samples and five compounds were observed in the TST samples but not in the SUMMA™ samples. Methyl alcohol was observed in the SUMMA™ samples but in only one TST sample. The compounds n-nitrosodimethylamine and pyrazine were observed in the TST samples but in only one SUMMA™ sample.

Table 2.1. Comparison of Mean Values for Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Triple Sorbent Traps and SUMMATM Canister Collected from the Headspace of Tank U-109 on 8/10/95

Target Analytes	CAS No.	S5055 ^(c) TST Results		S5055 ^(c) SUMMA TM Results		Relative Percent Difference %
		(mg/m ³)	St Dev	(mg/m ³)	St Dev	
Acetonitrile	75-05-8	0.08	0.01	0.03	0.01	91
Acetone	67-64-1	0.64	0.01	0.58	0.01	10
Trichlorofluoromethane	75-69-4	2.03	0.07	2.15	0.06	-6
Methylene Chloride	75-09-2	0.26	0.22	<0.02		na
Propanol	71-23-8	0.66	0.14	0.15	0.02	126
2-Butanone	78-93-3	0.08	0.00	0.09	0.01	-12
Hexane	110-54-3	0.07	0.01	0.06	0.00	15
Tetrahydrofuran	109-99-9	0.28	0.01	0.22	0.01	24
Benzene	71-43-2	0.05	0.00	0.04	0.01	22
Heptane	142-82-5	0.04	0.00	0.04	0.00	0
4-Methyl-2-Pentanone	108-10-1	0.04	(d)	<0.02		na
Toluene	108-88-3	0.17	0.01	0.14	0.01	19
Tetrachloroethylene	127-18-4	0.04	0.00	0.04	0.01	0
Ethylbenzene	100-41-4	0.03	0.00	0.03	0.00	0
p/m-Xylene ^(f)	106-42-3	0.12	0.01	0.11	0.01	9
o-Xylene	95-47-6	0.05	0.01	0.05	0.00	0
Butane	106-97-8	0.31	0.03	0.30	0.00	3
Pentane	109-66-0	0.10	0.01	0.09	0.01	11
1-Butanol	71-36-3	1.02	0.04	0.53	0.08	63
Tentatively Identified Compounds^(b)						
Propene	115-07-1	0.16	0.03	0.11	(d)	37
Propane	74-98-6	<0.02		0.26	0.01	na
Cyclopropane	75-19-4	<0.02		0.15	0.01	na
Ethane, 1-chloro-1,1-difluoro-	75-68-3	3.27	2.60	<0.04		na
Isobutane	75-28-5	<0.03		0.07	0.01	na
Methyl Alcohol	67-56-1	(e)		0.58	0.04	na
Propane, 2,2-dimethyl-	463-82-1	<0.03		0.11	0.00	na
Ethanol	64-17-5	0.89	0.07	0.30	0.01	99
Isopropyl Alcohol	67-63-0	<0.03		0.06	0.00	na
2-Propanol, 2-methyl-	75-65-0	0.09	(d)	<0.03		na
Butane, 2,2-dimethyl-	75-83-2	0.05	0.0	<0.04		na
N-Nitrosodimethylamine	62-75-9	0.23	0.02	(e)		na
Pyrazine	290-37-9	0.09	0.01	(e)		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) Compound observed above MDL in two SUMMATM/Triple Sorbent Trap Samples

(e) Compound observed above MDL in single SUMMATM/Triple Sorbent Trap Sample.

na Not applicable



3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank U-109 on August 10, 1995 (Sample Job S5055). 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 tracking of dilution/concentration of sample volumes obtained directly from the canisters. In the case of the sorbent traps, concentrations were based on analytical results and sample volumes reported by WHC. Known sampling and analytical variances from established quality assurance requirements, where significant, were documented in this report, as required by the Sampling and Analysis Plan (Homi 1995). An immediate notification (phone and electronic memo) was provided on August 18, 1995 after preliminary analytical results indicated the NH₃ concentration in Tank U-109 exceeded the notification level; notification levels and notification procedures are described in the Sampling and Analysis Plan (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

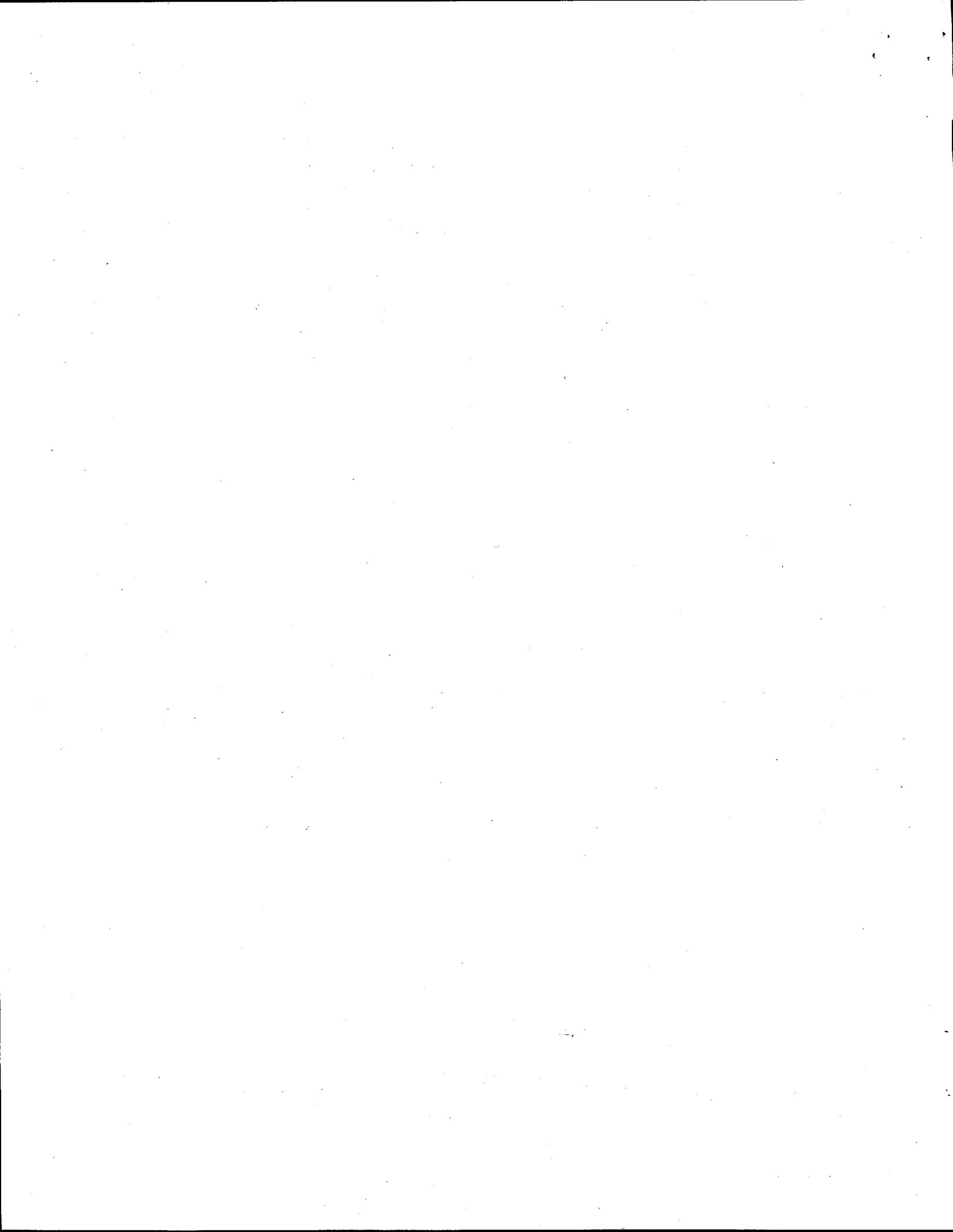
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Appendix A

Tank Vapor Characterization:

Inorganic Analytes



Appendix A

Tank Vapor Characterization: Inorganic Analytes

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to Westinghouse Hanford Company (WHC) for sampling the tank headspace using the Vapor Sampling System (VSS). Blanks, spiked blanks (when requested), and exposed samples were returned to Pacific Northwest National Laboratory (PNNL) for analysis. Analyses were performed to provide information on the tank headspace concentration of the following analytes: ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_2O). Procedures were similar to those developed previously during sample jobs performed with the VSS connected to the headspace of Tank C-103 (Ligotke et al. 1994). During those sample jobs, control samples provided validation that the 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 PNNL quality assurance (QA) impact level (IL) II requirements.

A.1 Sampling Methodology

Standard glass tubes containing sorbent materials to trap vapors of selected analytes of NH_3 , NO , NO_2 , and H_2O (supplied by SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for vapor sampling. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration to perform workplace monitoring and because of available procedures and verification results associated with that particular application. The typical sorbent traps used consisted of a glass tube containing a sorbent material specific to the compound of interest. In general, the tubes contained two sorbent layers, or sections; the first layer was the primary trap, and the second layer provided an indication of breakthrough. In the tubes, sorbent layers are generally held in packed layers separated by glass wool. The sorbent traps, 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 five or six samples, 5) continuing this sequence until all samples of the batch have been measured, including duplicates and spiked samples, and 6) remeasuring the complete set of calibration standards (at the end of the session). 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) one guard column (AG4A) and two separator columns (AS4A) in series instead of just one 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 one of the midrange standards was

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- (a) Procedure entitled "Ammonia (Nitrogen) in Aqueous Samples," PNL-ALO-226, in the *Analytical Chemistry Laboratory (ACL) Procedure Compendium*, Vol. 3: Inorganic Instrumental Methods. Pacific Northwest Laboratory, Richland, Washington.
- (b) Procedure entitled "Determination of Inorganic Anions by Ion Chromatography," PNL-ALO-212, in the *Analytical Chemistry Laboratory (ACL) Procedure Compendium*, Vol. 3: Inorganic Instrumental Methods. Pacific Northwest Laboratory, Richland, Washington.

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

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

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

A.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNNL documents. The samples were analyzed following PNNL Impact Level II. The PNNL documents include PNL-MA-70 (Part 2), PNL-ALO-212, PNL-ALO-226, and MCS-046. A summary of the analysis procedures and limits for the target inorganic compounds is provided in Table A.1. The table also shows generic expected notification ranges and describes related target analytical precision and accuracy levels for each analyte; the information in the table is based on the data quality objective assessment by Osborne et al. (1995). From the table, it can be seen that the method detection limit (MDL) required to resolve the analyte at one-tenth of the recommended exposure limit for each of the target analytes is achieved using current procedures and with a vapor-sample volume of 3 L and a desorption-solution volume of 3 mL (10 mL for NH_3).

The accuracy of concentration measurements depends on potential errors associated with both sampling and analysis (see Section A.4). Sampling information, including sample volumes, was provided by WHC; sample-volume uncertainty was not provided. The uncertainty of analytical results, which depends on the method used, was estimated to be within allowable tolerances (Osborne et al. 1995; Table A.1). For NH_3 analyses, the accuracy of laboratory measurements by selective ion electrode was estimated to be $\pm 5\%$ relative, independent of concentration at $1 \mu\text{g/mL}$ 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>	<u>MDL^(b) (μg)</u>	<u>MDL^(b) (ppmv)</u>	<u>Expected Range^(c) (ppmv)</u>	<u>Notification Level^(c) (ppmv)</u>
Ammonia	NH ₃	PNL-ALO-226	0.1	0.5	≥ 2	≥ 150
Nitrogen Dioxide	NO ₂	PNL-ALO-212	0.02	0.02	≥ 0.1	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.02	0.02	≥ 2	≥ 50
Mass (water) ^(d)	n/a	PNL-TVP-09	0.6 mg	0.2 mg/L	≥ 3 mg/L	n/a

- (a) Analytical precision and accuracy targets for results in the expected ranges equal $\pm 25\%$ 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 four 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.
n/a = not applicable.

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

A.4 Inorganic Sample Results

Samples were obtained by WHC from the tank headspace of Tank U-109 on August 10, 1995 using the VSS. The sample job designation number was S5055. Samples were prepared, submitted to WHC for the sample job, and then returned to PNNL and analyzed to provide information on the concentrations of NH₃, NO₂, NO, and mass (primarily H₂O). Samples were controlled using chain-of-custody 009253 (Appendix F). The inorganic samples were received from WHC on August 14, 1995; the sample volume information was received on August 11, 1995. Analyses were completed on August 16, 1995 (gravimetric, 6-day hold time), August 17, 1995 (ammonia, 7-day hold time), and August 18, 1995 (nitrite, 8-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, a NO_x series in the middle (Section A.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table A.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank headspace concentration results (Table A.3) are based on this information, and the listed uncertainties equal plus or minus one standard deviation of

the individual results from each set of samples. Percentage relative standard deviation (RSD) may be determined by dividing the standard deviation by the average result and multiplying by 100. Where analytical results from samples 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 577 ± 20 ppmv, based on all six samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 74.8 to 79.5 μmol in front sections; NH_3 was not found ($\leq 0.01 \mu\text{mol}$) in back sorbent sections. Blank corrections, $\leq 0.08 \mu\text{mol}$ in front and $\leq 0.04 \mu\text{mol}$ in back sections, were about 0.2% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of $\pm 5\%$. One sample leachate was spiked after initial analysis with roughly the quantity of NH_3 in the sample and yielded a percentage recovery of 96%. The continuing calibration verification standard, using NIST-traceable material, yielded percentage recoveries of 100, 108, and 108% during the analytical session. A five-point calibration was performed over an NH_3 range of 0.1 to 1000 $\mu\text{g/mL}$. Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 $\mu\text{mol NH}_3$ were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively, during previous sample jobs (Clauss et al. 1994; Ligotke et al. 1994).

A.4.2 Nitrogen Oxides Results. It is not known whether the presence of an upstream NH_3 trap typically affects downstream measurements of NO_2 and NO . Consequently, measurements of NO_2 and NO were made using four "protected" five-segment $\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ and two "unprotected" four-segment $\text{NO}_x/\text{H}_2\text{O}$ sorbent-trap trains. (The NO_x trains consisted of three segments: NO_2 trap, oxidizer, NO_2 trap.) Although NO results were potentially greater from unprotected samples, no further comparison was possible because of the small quantities of nitrite in the samples. Because of this uncertainty, measurements using the two types of sorbent trap trains are planned to be continued during subsequent sample jobs for which NO_x measurements are required. No further evaluation is required of the results from this sample job.

The concentrations of NO_2 and NO were both ≤ 0.06 ppmv, respectively, based on all six samples. Blank-corrected NO_2^- quantities in the sorbent traps averaged $\leq 0.0039 \mu\text{mol}$ (NO_2 samples) and $\leq 0.0039 \mu\text{mol}$ (NO samples). Nitrite blank levels used to correct data were $0.0048 \pm 0.0016 \mu\text{mol}$ in front (three of six blanks analyzed) and $0.0023 \pm 0.0005 \mu\text{mol}$ in back (two of six blanks analyzed) sorbent sections. The analyses of four samples were duplicated and all yielded repeatabilities of $\pm 1\%$ and $\pm 2\%$. Four sample leachates were spiked with 0.25 ppm NO_2^- and yielded percentage recoveries of 101%, 97%, 97%, and 92%. A four-point calibration was performed over a concentration range of 0 to 0.5 $\mu\text{g NO}_2^-$ per mL in the desorbing matrix. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 $\mu\text{mol NO}_2^-$ during previous sample jobs yielded percentage recoveries of $153 \pm 14\%$, $103 \pm 4\%$, $106 \pm 8\%$, and $111 \pm 7\%$, respectively (Clauss et al. 1994; Ligotke et al. 1994).

Table A.2. List of PNNL Inorganic Samples, Controls, and Gravimetric Results Obtained from a Heated Tube Inserted into the Headspace of Tank U-109 on 08/10/95

<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>						
S5055-A08-77T	NH ₃ /NO _x /H ₂ O Train	5	200.0	15.0	3.00	0.0462
S5055-A09-78T	NH ₃ /NO _x /H ₂ O Train	6	200.0	15.0	3.00	0.0460
S5055-A10-79T	NO _x /H ₂ O Train	7	189.9	15.0	2.85	0.0439
S5055-A11-80T	NH ₃ /H ₂ O/H ₂ O Train	8	193.8	15.0	2.91	0.0443
S5055-A16-81T	NH ₃ /NO _x /H ₂ O Train	5	200.0	15.0	3.00	0.0461
S5055-A17-82T	NH ₃ /NO _x /H ₂ O Train	6	200.0	15.0	3.00	0.0454
S5055-A18-83T	NO _x /H ₂ O Train	7	188.7	15.0	2.83	0.0404
S5055-A19-84T	NH ₃ /H ₂ O/H ₂ O Train	8	193.8	15.0	2.91	0.0438
<u>Controls:</u>						
S5055-A25-85T	NH ₃ /NO _x /H ₂ O Field Blank	n/a ^(b)	n/a	n/a	n/a	0.0011
S5055-A26-86T	NH ₃ /NO _x /H ₂ O Field Blank	n/a	n/a	n/a	n/a	0.0008
S5055-A27-87T	NH ₃ /NO _x /H ₂ O Field Blank	n/a	n/a	n/a	n/a	0.0015

(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 four- and five-trap sorbent trains, believed to be primarily water vapor, was 14.8 ± 0.4 mg/L. The result was based on an average mass gain of 43.4 mg from all eight (NH₃/NO_x/H₂O and NO_x/H₂O) sample trains. The blank correction applied to the results was - 1.1 mg per train, based on a mass gain of 1.1 ± 0.4 mg per three five-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of ± 0.1 mg. Although no spiked blanks were tested, the percentage recovery of mass from three blank 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 U-109 on 08/10/95

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor ^(b) Concentration (ppmv)
	Front Section	Back Section	Total ^(a) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>11.9^(c)</u>	<u>2.97^(c)</u>	<u>577 ± 20^(c)</u>
S5055-A08-77T	76.0	0.04	75.9	3.00	567
S5055-A09-78T	74.8	NA ^(d)	74.8	3.00	558
S5055-A11-80T	72.3	0.05	72.2	2.91	556
S5055-A16-81T	78.1	NA	78.0	3.00	583
S5055-A17-82T	79.3	0.05	79.5	3.00	592
S5055-A19-84T	79.0	NA	78.9	2.91	608
<u>NO₂ Samples:</u>			<u>≤ 0.0039</u>	<u>2.95</u>	<u>≤ 0.06</u>
S5055-A08-77T	0.0064	0.0025	n/a ^(d)	3.00	n/a
S5055-A09-78T	0.0067	NA	n/a	3.00	n/a
S5055-A10-79T ^(e)	0.0050	0.0019	n/a	2.85	n/a
S5055-A16-81T	0.0072	0.0028	n/a	3.00	n/a
S5055-A17-82T	0.0064	NA	n/a	3.00	n/a
S5055-A18-83T ^(e)	0.0050	0.0023	n/a	2.83	n/a
<u>NO Samples:</u>			<u>≤ 0.0039</u>	<u>2.95</u>	<u>≤ 0.06</u>
S5055-A08-77T	0.0053	NA	n/a	3.00	n/a
S5055-A09-78T	0.0052	0.0028	n/a	3.00	n/a
S5055-A10-79T ^(e)	0.0083	0.0023	n/a	2.85	n/a
S5055-A16-81T	0.0051	NA	n/a	3.00	n/a
S5055-A17-82T	0.0048	0.0026	n/a	3.00	n/a
S5055-A18-83T ^(e)	0.0086	0.0027	n/a	2.83	n/a
<u>Gravimetric Samples:</u>			<u>43.4 mg</u>	<u>2.94</u>	<u>14.8 ± 0.4 mg/L</u>
S5055-A08-77T	n/a	n/a	45.1	3.00	15.0
S5055-A09-78T	n/a	n/a	44.9	3.00	15.0
S5055-A10-79T	n/a	n/a	42.8	2.85	15.0
S5055-A11-80T	n/a	n/a	43.2	2.91	14.8
S5055-A16-81T	n/a	n/a	45.0	3.00	15.0
S5055-A17-82T	n/a	n/a	44.3	3.00	14.8
S5055-A18-83T	n/a	n/a	39.3	2.83	13.9
S5055-A19-84T	n/a	n/a	42.7	2.91	14.7

- (a) Total blank-corrected analyte masses (nitrite for NO₂ and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The level of analytes found in blanks is described in the subsections of Section A.4.
- (b) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (Table A.2). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrate. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks.
- (c) Underlined values represent the average of the set samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. Percent RSD may be determined by dividing standard deviation by the average and multiplying by 100. The use of "≤" is defined in Section A.4.
- (d) NA = not analyzed; n/a = not applicable.
- (e) NO_x sorbent traps not preceded by an NH₃ trap. Only selected back sorbent sections were analyzed. Results show back sections of ammonia and nitrite samples contain insignificant quantities of the analytes.

A.5 References

Clauss, T. W., M. W. 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.

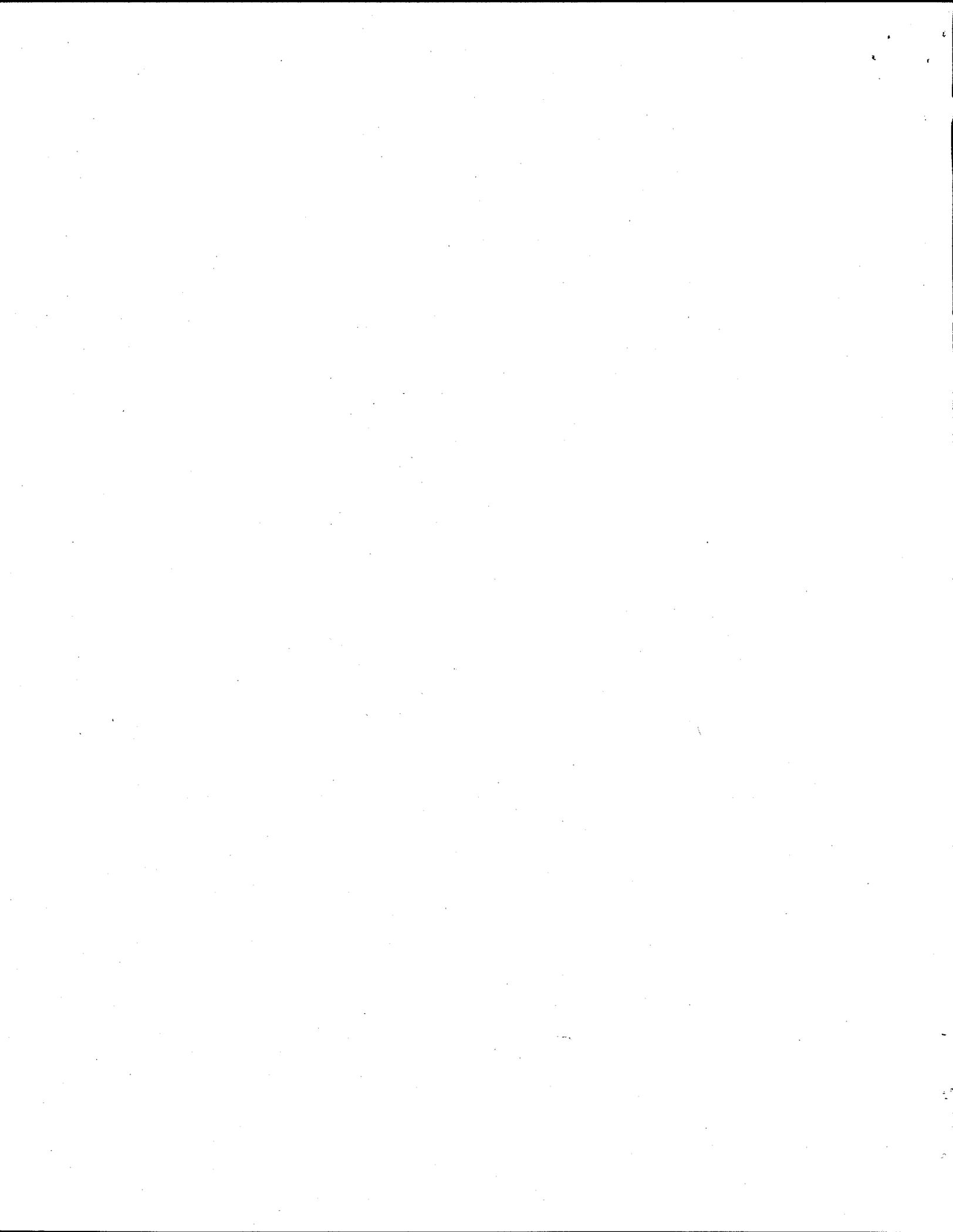
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Appendix B

Tank Vapor Characterization:

Permanent Gases



Appendix B

Tank Vapor Characterization: Permanent Gases

B.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNNL Technical Procedure PNL-TVP-01^(b), which is a modification of U.S. Environmental Protection Agency (EPA) compendium Method TO-14. If the canister is verified as clean and free of TO-14 and unknown contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 µL of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

B.2 Analytical Procedure

The SUMMA™ canister samples were analyzed for permanent gases according to PNNL 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 method detection limits (MDLs) used 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. An MDL for the instrument has not been determined. The lowest calibration standard for each analyte is reported as the MDL. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within $\pm 25\%$ of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N₂ reagent blank, an ambient-air sample collected ~ 10 m upwind of Tank U-109, and the ambient air collected through the Vapor Sampling System (VSS) were used as method blanks and used to determine the potential for analyte interferences in the samples.

B.4 Permanent Gases Sample Results

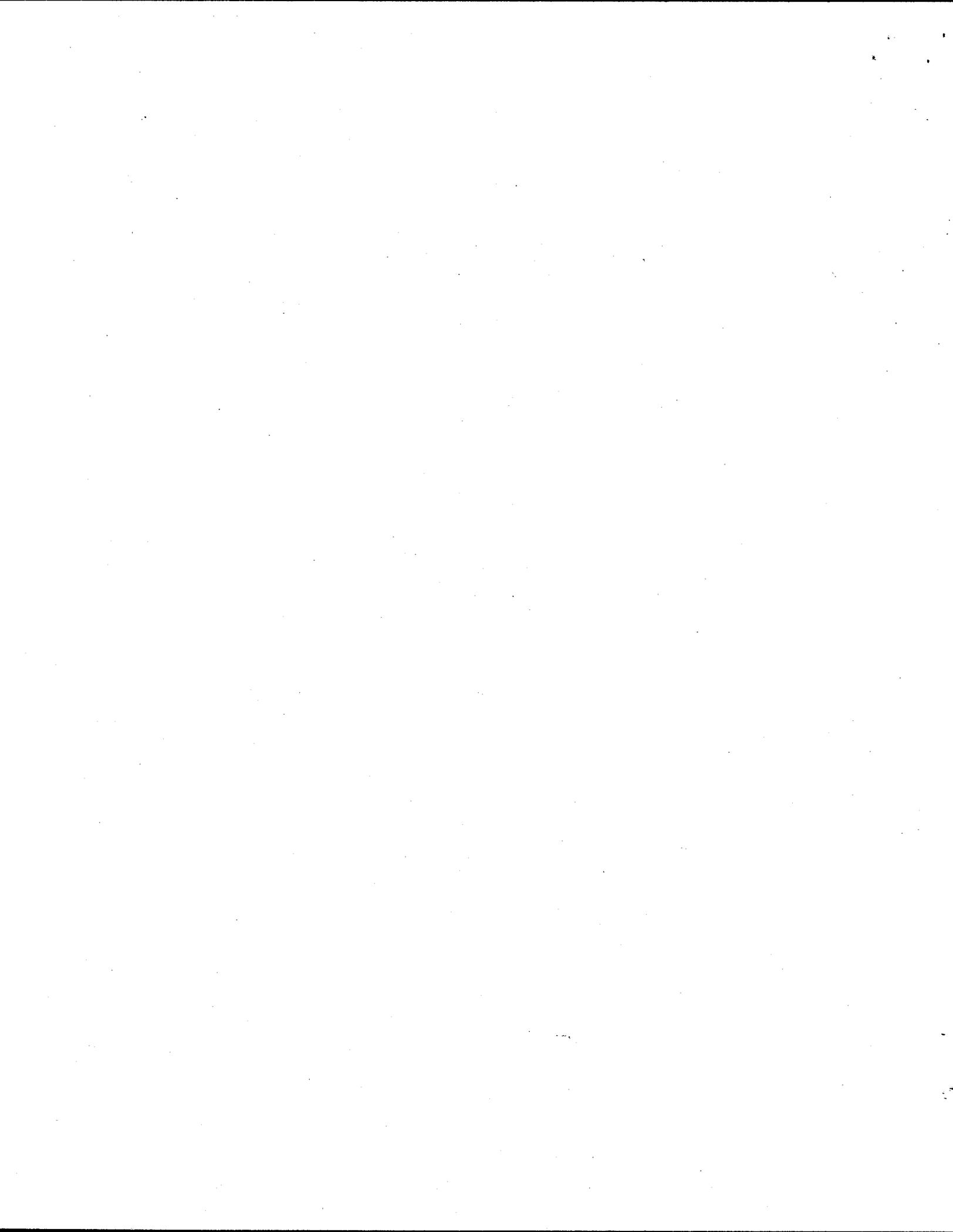
Table B.2 lists results of the permanent gas analysis from samples collected from the headspace of Tank U-109, ambient air collected ~ 10 m upwind of the tank, and ambient air collected through the VSS. The samples were analyzed on August 16, 1995. Hydrogen (748 ppmv) and nitrous oxide (868 ppmv) were observed above the MDL in the tank headspace samples. Carbon dioxide in the headspace was at a lower concentration than observed in the ambient air. A duplicate analysis was performed on SUMMA™ canister PNL 254; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

Table B.2. Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank U-109 and for Ambient Air and Ambient Air Through the VSS Collected Near Tank U-109 in SUMMA™ Canisters on 8/10/95

<u>Sample</u>	<u>Sample Matrix</u>	<u>PNNL Canister Number</u>	<u>Sample Concentration (ppmv)</u>	<u>Average Concentration (ppmv)^(a)</u>
<u>CO₂ Samples:</u>				
S5055-A04-252	Tank	252	<25	<25
S5055-A12-254	Tank	254	<25	
S5055-A20-255	Tank	255	<25	
S5055-A12-254	Tank ^(b)	254	<25	
S5055-A01-213	Ambient Air - Upwind	213	350	
S5055-A02-251	Ambient Air - VSS	251	342	
<u>CO Samples:</u>				
S5055-A04-252	Tank	252	<25	<25
S5055-A12-254	Tank	254	<25	
S5055-A20-255	Tank	255	<25	
S5055-A12-254	Tank ^(b)	254	<25	
S5055-A01-213	Ambient Air - Upwind	213	<25	
S5055-A02-251	Ambient Air - VSS	251	<25	
<u>CH₄ Samples:</u>				
S5055-A04-252	Tank	252	<25	<25
S5055-A12-254	Tank	254	<25	
S5055-A20-255	Tank	255	<25	
S5055-A12-254	Tank ^(b)	254	<25	
S5055-A01-213	Ambient Air - Upwind	213	<25	
S5055-A02-251	Ambient Air - VSS	251	<25	
<u>H₂ Samples:</u>				
S5055-A04-252	Tank	252	724	748
S5055-A12-254	Tank	254	749	
S5055-A20-255	Tank	255	770	
S5055-A12-254	Tank ^(b)	254	758	
S5055-A01-213	Ambient Air - Upwind	213	<25	
S5055-A02-251	Ambient Air - VSS	251	<25	
<u>N₂O Samples:</u>				
S5055-A04-252	Tank	252	873	868
S5055-A12-254	Tank	254	876	
S5055-A20-255	Tank	255	855	
S5055-A12-254	Tank ^(b)	254	859	
S5055-A01-213	Ambient Air - Upwind	213	<25	
S5055-A02-251	Ambient Air - VSS	251	<25	

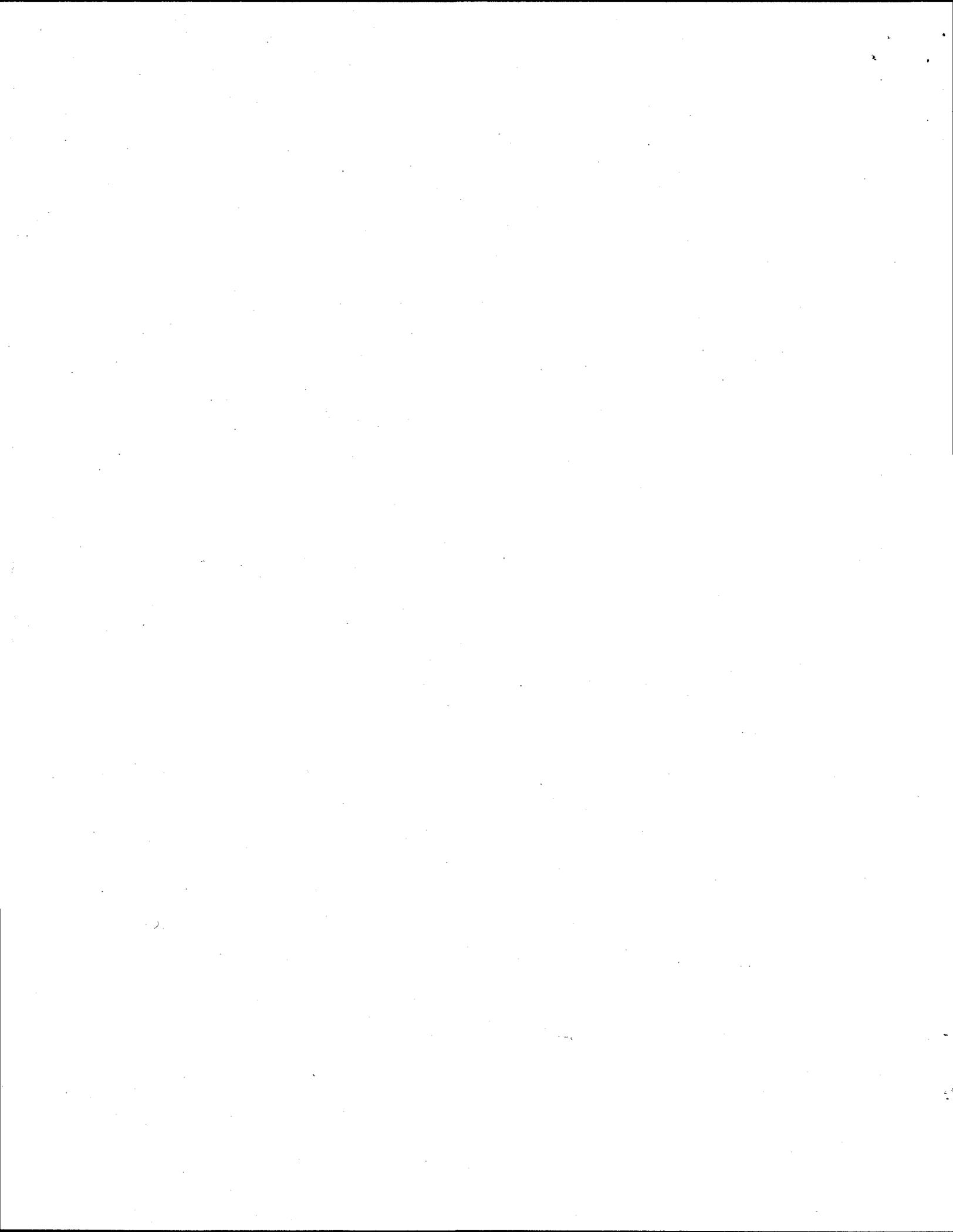
(a) Average concentrations are reported for the tank matrix and do not include duplicate analysis results or the ambient-air results.

(b) Analytical duplicate of tank sample used to determine analytical precision.



Appendix C

Tank Vapor Characterization: Total Non-Methane Hydrocarbons



Appendix C

Tank Vapor Characterization: Total Non-Methane Hydrocarbons

C.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant-free according to Pacific Northwest National Laboratory (PNNL) 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 PNNL 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 PNNL 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 nonmethane 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 five-point, multi-level, linear regression curve.

A NIST 3-parts per million by volume (ppmv) propane standard is analyzed as a calibration check with appropriate blanks and samples run subsequently. The initial calibration is used to quantify the samples.

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

Before the tank samples were analyzed, a diagnostic check was performed on the GC/FID instrument by running a system cleanliness procedure and an instrument continuing calibration as described in PNL-TVP-08. First, two blank volumes of Aadco purified air were analyzed to check the cleanliness of the system. This demonstrates through the analysis of a zero-air blank that the level of interference is acceptable in the analytical system. The system should be cleaned to 0.1 mg/m³ of TNMOCs. Second, an instrument continuing calibration run using 100-mL UHP propane analyzed using the response factor as an external standard method, followed by one blank volume of Aadco air.

C.3.1 Quantitation Results of Target Analytes. The mg/m³ was derived from the five-point multilevel calibration curve from the propane standard using the following equation:

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

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

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

C.4 Total Non-Methane Hydrocarbons Sample Results

Table C.1 lists results of the TO-12 gas analysis from samples collected from the headspace of Tank U-109, ambient air collected ~ 10 m upwind of the tank, and ambient air collected through the vapor sampling system. The samples were analyzed on August 30, 1995. Concentrations in the ambient-air samples ranged from 0.28 mg/m³ to 0.36 mg/m³. Concentrations in the three tank headspace samples ranged from 8.75 mg/m³ to 9.67 mg/m³ with an average concentration of 9.25 mg/m³. This compares to 6.49 mg/m³ for the sum of all compounds identified in the target and tentatively identified compound (TIC) analysis of the SUMMA™ canisters. A replicate analysis was performed on SUMMA™ canister PNL 254; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

Table C.1. TO-12 Results for Samples Collected from the Headspace of Tank U-109 and for Ambient Air and Ambient Air Through the VSS Collected near Tank U-109 in SUMMA™ Canisters on 8/10/95

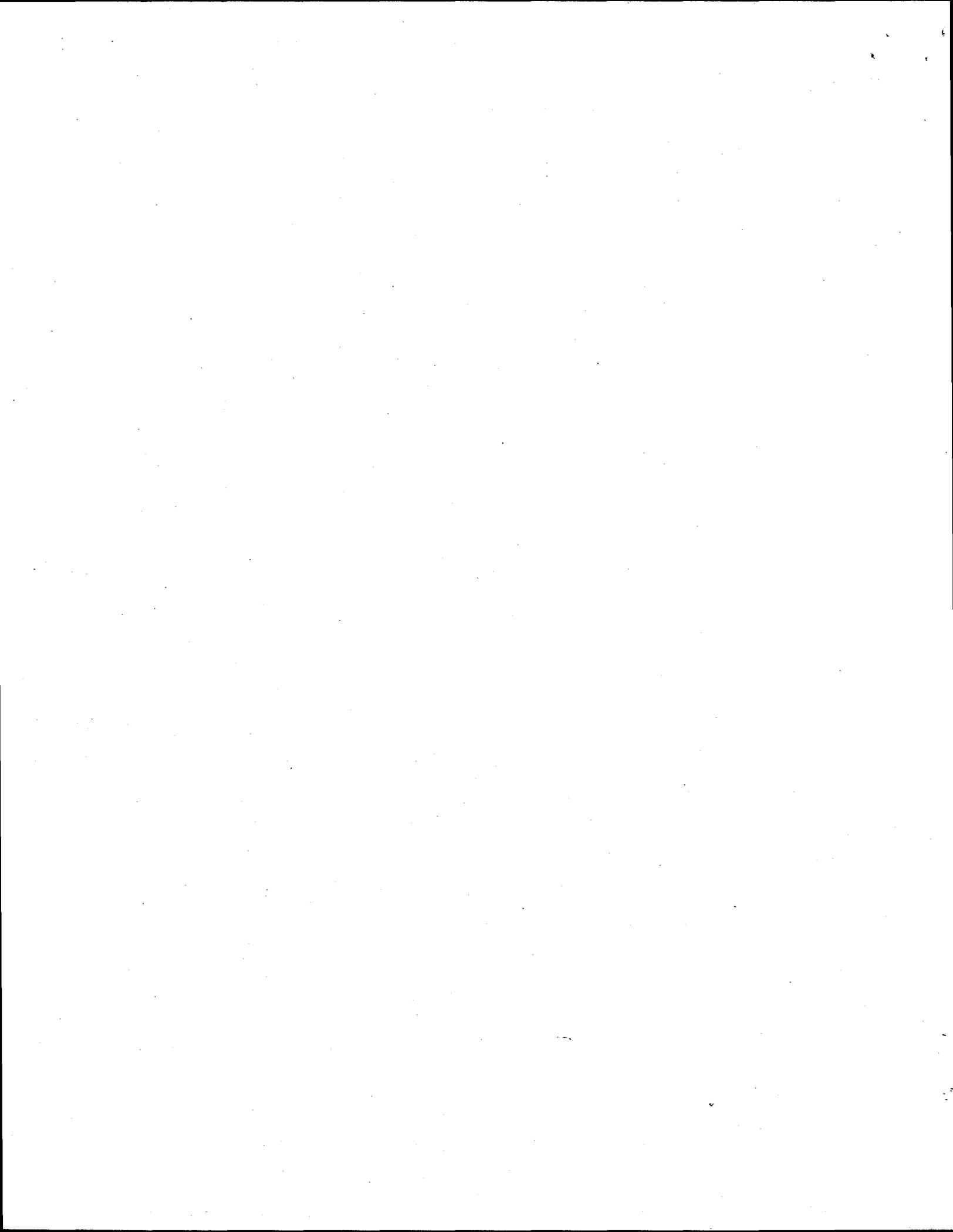
Ambient Air Upwind		Ambient Air Through VSS		Tank Samples			Average Concentration Tank Samples
SS-055-A01.213 ^(a)	PNL 213 ^(b)	SS-055-A02.251 ^(a)	PNL 251 ^(b)	SS-055-A04.252 ^(a)	PNL 252 ^(b)	SS-055-A12.254 ^(a)	PNL 254 ^{(b)(c)}
Concentration	(mg/m ³)						
0.36		0.28		9.32		8.75	
						9.67	
						10.04	
							9.25

(a) WHC sample identification number.
 (b) PNL canister number.
 (c) Replicate analysis for PNL 254; results are not included in the calculation of average concentrations.

Appendix D

Tank Vapor Characterization:

Volatile Organic Analytes



Appendix D

Tank Vapor Characterization: Volatile Organic Analytes

D.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to Pacific Northwest National Laboratory (PNNL) 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 PNNL 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 μ L of distilled water and labeled with a field-sampling identification. Cleaned canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

D.2 Analytical Procedure

The SUMMA™ canister sample was analyzed according to PNNL Technical Procedure PNL-TVP-03^(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 chromatograph/mass spectrometer (GC/MS). The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate the air volume, then transfer the volume to the GC/MS for analysis. A 100-mL volume of sample is measured and analyzed from the tank headspace. The organic components in the sampled air are separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm internal diameter with 3- μ m 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

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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.

was first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level exactly twice the original pressure. For example, if the canister had a starting pressure of 740 torr, it was pressurized to 1480 torr. This dilution was an effort to improve the precision of the analysis. The sample dilution was taken into account when calculating the analysis results.

The instrument calibration mixture for the PNL-TVP-03 analysis consists of 62 compounds. These 62 compounds that are directly quantified in this analysis make up the target analyte list (these 62 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table D.1. The calibration mixture was prepared by blending a commercially prepared TO-14 calibration mixture with a mixture created using a Kin-Tek® permeation-tube standard generation system. The operation of the permeation-tube system follows the method detailed in PNNL Technical

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	Butane
Pentane	1-Butanol
Octane	Nonane
Undecane	Dodecane
Tridecane	Tetradecane

Procedure PNL-TVP-06^(a). The standard calibration mix was analyzed using four aliquot sizes ranging from 30 mL to 200 mL, and a response factor for each compound was calculated. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. Performance-based detection limits for the target analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 ppbv is used.

D.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "high-sensitivity tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated using a standard gas mixture containing 62 organic compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d₅, 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 searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

(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.

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:

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

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/m³ and the molecular weight of the analyte.

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

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-d₅, and 104 ppbv for bromofluorobenzene. The IS concentrations were converted from ppbv to mg/m³ at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, 117.6 for chlorobenzene-d₅, and 175.00 for bromofluorobenzene. All calculated sample concentrations were multiplied by a factor of two to account for the dilution step described in Section D.2.

D.4 Volatile Organic Sample Results

Five SUMMA™ canisters were returned to the laboratory on August 14, 1995 under Westinghouse Hanford Company (WHC) chain-of-custody 009251 (see Appendix F). The samples were analyzed on September 21 and 22, 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 U-109 and through the VSS near Tank U-109 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. Seventeen target analytes above the 5-ppbv reporting cutoff and 12 TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. All target analytes and 11 TICs were identified in two or more tank headspace samples. Trichlorofluoromethane (2.15 mg/m³), acetone (0.58 mg/m³), and 1-butanol (0.53 mg/m³) accounted for 70% of the target analytes and 50% of the total concentration identified by both the target and TIC analyses. The total concentration of the target analytes was found to be 4.65 mg/m³. Methyl alcohol (0.58 mg/m³), ethanol (0.30 mg/m³), and propane (0.26 mg/m³) accounted for 62% of the TICs and 18% of the total concentrations identified by both the target and TIC analyses. The total concentration of TICs found was 1.84 mg/m³. The total concentration of all the compounds identified was 6.49 mg/m³. This compares to a total concentration of 9.25 mg/m³ identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 254 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. Fifteen of 17 target analytes and 9 of 10 TICs had RPDs of less than 10%.

Table D.4 lists the quantitative results for compounds listed as target analytes and TICs in ambient air and ambient air through the vapor sampling system. Pyridine and 2-butanone were the only target analytes observed in the ambient-air sample. No target analytes were observed in the ambient air through the VSS sample. No TICs were observed in the two ambient-air samples.

The percent relative standard deviation for all target compounds in the initial calibration met the 30% acceptance criterion. The relative response factors for all target compounds met the 30% acceptance criterion for percent difference in both continuing calibration verification runs. No compounds exceeding 5 ppbv were found in any of the blanks that bracketed either standards or tank samples.

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 U-109 in SUMMA™ Canisters collected on 8/10/95

Target Analytes ^(a)	CAS No.	Mol Wt	Ret Time	S5055-A04.252 ^(c)		S5055-A12.254 ^{(c)(d)}		S5055-A20.255 ^(e)		Mean and Standard Deviations ^(b)	
				PNL 252 ^(e) (mg/m ³) (ppbv)	PNL 254 ^{(c)(e)} (mg/m ³) (ppbv)	PNL 254 ^{(c)(e)} (mg/m ³) (ppbv)	PNL 255 ^(e) (mg/m ³) (ppbv)	(mg/m ³) St Dev	(ppbv) St Dev		
Acetonitrile	75-05-8	41.1		0.02	0.03	0.03	0.03	0.01	0.01	14	0.7
Acetone	67-64-1	58.1		0.57	0.59	0.57	0.57	0.01	0.01	223	3.4
Trichlorofluoromethane	75-69-4	137.4		2.19	2.18	2.08	2.08	0.06	0.06	350	9.7
Propanol	71-23-8	60.1		0.14	0.17	0.15	0.15	0.02	0.02	57	6.1
2-Butanone	78-93-3	72.1		0.08	0.09	0.09	0.09	0.01	0.01	26	1.8
Hexane	110-54-3	86.2		0.06	0.06	0.06	0.06	0.00	0.00	16	0.2
Tetrahydrofuran	109-99-9	72.1		0.22	0.22	0.23	0.23	0.01	0.01	69	1.8
Benzene	71-43-2	78.1		0.04	0.04	0.05	0.05	0.01	0.01	13	0.9
Heptane	142-82-5	100.2		0.04	0.04	0.04	0.04	0.00	0.00	9	0.3
Toluene	108-88-3	92.1		0.14	0.14	0.15	0.15	0.01	0.01	35	1.5
Tetrachloroethylene	127-18-4	165.8		0.04	0.04	0.05	0.05	0.01	0.01	6	0.4
Ethylbenzene	100-41-4	106.2		0.03	0.03	0.03	0.03	0.00	0.00	6	0.4
p/n-Xylenes ^(a)	106-42-3	106.2		0.10	0.11	0.11	0.11	0.01	0.01	23	1.4
o-Xylenes	95-47-6	106.2		0.05	0.05	0.05	0.05	0.00	0.00	10	0.5
Butane	106-97-8	58.1		0.30	0.30	0.30	0.30	0.00	0.00	116	1.2
Pentane	109-66-0	72.2		0.10	0.09	0.09	0.09	0.01	0.01	28	1.6
1-Butanol	71-36-3	74.1		0.47	0.50	0.62	0.62	0.08	0.08	160	24
Tentatively Identified Compound^(b)											
Propene	115-07-1	42	4.2	0.152	<0.02	0.065	0.065	(g)	(g)	58	(g)
Propane	74-98-6	44	4.3	0.256	0.256	0.265	0.265	0.01	0.01	132	2.6
Cyclopropane	75-19-4	42	4.8	0.153	0.144	0.155	0.155	0.01	0.01	80	3.1
Isobutane	75-28-5	58	5.0	0.064	0.063	0.073	0.073	0.01	0.01	26	2.1
Methyl Alcohol	67-56-1	32	5.2	0.563	0.561	0.625	0.625	0.04	0.04	408	25
Unknown Alkene		56	5.5	0.085	0.083	0.091	0.091	0.00	0.00	35	1.7
Propane, 2,2-dimethyl-	463-82-1	72	6.0	0.107	0.106	0.106	0.106	0.00	0.00	33.1	0.2
Unknown Alkene		56	6.1	0.064	0.060	0.063	0.063	0.00	0.00	24.9	0.8
Ethanol	64-17-5	46	6.8	0.296	0.304	0.292	0.292	0.01	0.01	145	3.0

U-109 Table D.2. (Contd)

Tentatively Identified Compound ^(a)	CAS No.	Mol Wt	Ret Time	S5055-A04.252 ^(c)		S5055-A12.254 ^{(e)(f)}		S5055-A20.255 ^(e)		Mean and Standard Deviations ^(b)	
				PNL 252 ^(e) (mg/m ³) (ppbv)	PNL 254 ^{(f)(e)} (mg/m ³) (ppbv)	PNL 254 ^{(f)(e)} (mg/m ³) (ppbv)	PNL 255 ^(e) (mg/m ³) (ppbv)	(mg/m ³) St Dev	(ppbv) St Dev		
Isopropyl Alcohol	67-63-0	60	8.2	0.054	0.06	0.062	23	0.06	0.00	21.9	1.6
N-Nitrosodimethylamine	62-75-9	74	19.7	0.047	0.051	0.062	19	0.05	0.01	16.1	2.4
Pyrazine	290-37-9	80	19.9	<0.04	<0.04	0.055	15	(g)	(g)	(g)	(g)

- (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 EPANIST and WILEY Libraries.
- (g) Mean and/or standard deviation are not meaningful for this analyte.
- (h) Mean and standard deviations based on analytical values reported to two or three decimal places, not face values reported in table.
- (i) Target analyte ppb values reported to two decimal places, but rounded to the whole integer in individual SUMMA canister results.
- (j) m-Xylene and p-Xylene coelute; the reported concentration is the sum of these two compounds.

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 U-109 on 8/10/95

Target Analytes	CAS No.	Mol Wt.	Ret Time	S5055-A12.254 ^(c)		S5055-A12.254 ^(c)		Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	
Acetonitrile	75-05-8	41.1		0.03	14	0.03	15	0
Acetone	67-64-1	58.1		0.59	226	0.62	240	5
Trichlorofluoromethane	75-69-4	137.4		2.18	355	2.19	357	0
Propanol	71-23-8	60.1		0.17	64	0.15	55	13
2-Butanone	78-93-3	72.1		0.09	27	0.09	29	0
Hexane	110-54-3	86.2		0.06	16	0.06	17	0
Tetrahydrofuran	109-99-9	72.1		0.22	70	0.23	72	4
Benzene	71-43-2	78.1		0.04	13	0.05	13	22
Heptane	142-82-5	100.2		0.04	9	0.04	9	0
Toluene	108-88-3	92.1		0.14	35	0.15	36	7
Tetrachloroethylene	127-18-4	165.8		0.04	6	0.04	6	0
Ethylbenzene	100-41-4	106.2		0.03	6	0.03	6	0
p/m-Xylene	106-42-3	106.2		0.11	23	0.11	23	0
o-Xylene	95-47-6	106.2		0.05	10	0.05	10	0
Butane	106-97-8	58.1		0.30	116	0.31	118	3
Pentane	109-66-0	72.2		0.09	28	0.09	29	0
1-Butanol	71-36-3	74.1		0.50	151	0.54	162	8
Tentatively Identified Compound^(e)								
Propene	115-07-1	42	4.2	<0.02	<10	<0.02	<10	4
Propane	74-98-6	44	4.3	0.256	130	0.267	136	5
Cyclopropane	75-19-4	42	4.8	0.144	77	0.151	81	6
Isobutane	75-28-5	58	5.0	0.063	24	0.067	26	0
Methyl Alcohol	67-56-1	32	5.2	0.561	393	0.562	393	7
Unknown Alkene		56	5.5	0.083	33	0.089	36	4
Propane, 2,2-dimethyl-	463-82-1	72	6.0	0.106	33	0.110	34	5
Unknown Alkene		56	6.1	0.060	24	0.063	25	4
Ethanol	64-17-5	46	6.8	0.304	148	0.317	154	0
Isopropyl Alcohol	67-63-0	60	8.2	0.060	22	0.060	22	11
N-Nitrosodimethylamine	62-75-9	74	19.7	0.051	15	0.057	17	
Pyrazine	290-37-9	80	19.9	<0.04	<10	<0.04	<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 SUMMATM canister number.

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

(f) Relative percent differences (RPDs) based on mg/m³ values; target analyte RPDs based on analytical values reported to two decimal places; TIC RPDs are based on analytical values reported to three decimal places.

Table D.4. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified and Estimated Concentrations^(b) in Ambient Air and Ambient Air Through the VSS Collected Near Tank U-109 in SUMMA™ Canisters on 8/10/95

<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>	
				<u>(mg/m³)</u>	<u>(ppbv)</u>	<u>(mg/m³)</u>	<u>(ppbv)</u>
2-Butanone	78-93-3	72.11		0.03	9	<0.02	<5
Pyridine	110-86-1	79.1		0.03	8	<0.02	<5
				<u>PNL 213^(c)</u>		<u>PNL 251^(d)</u>	

Tentatively

Identified Compound^(b)
No Compounds Identified

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

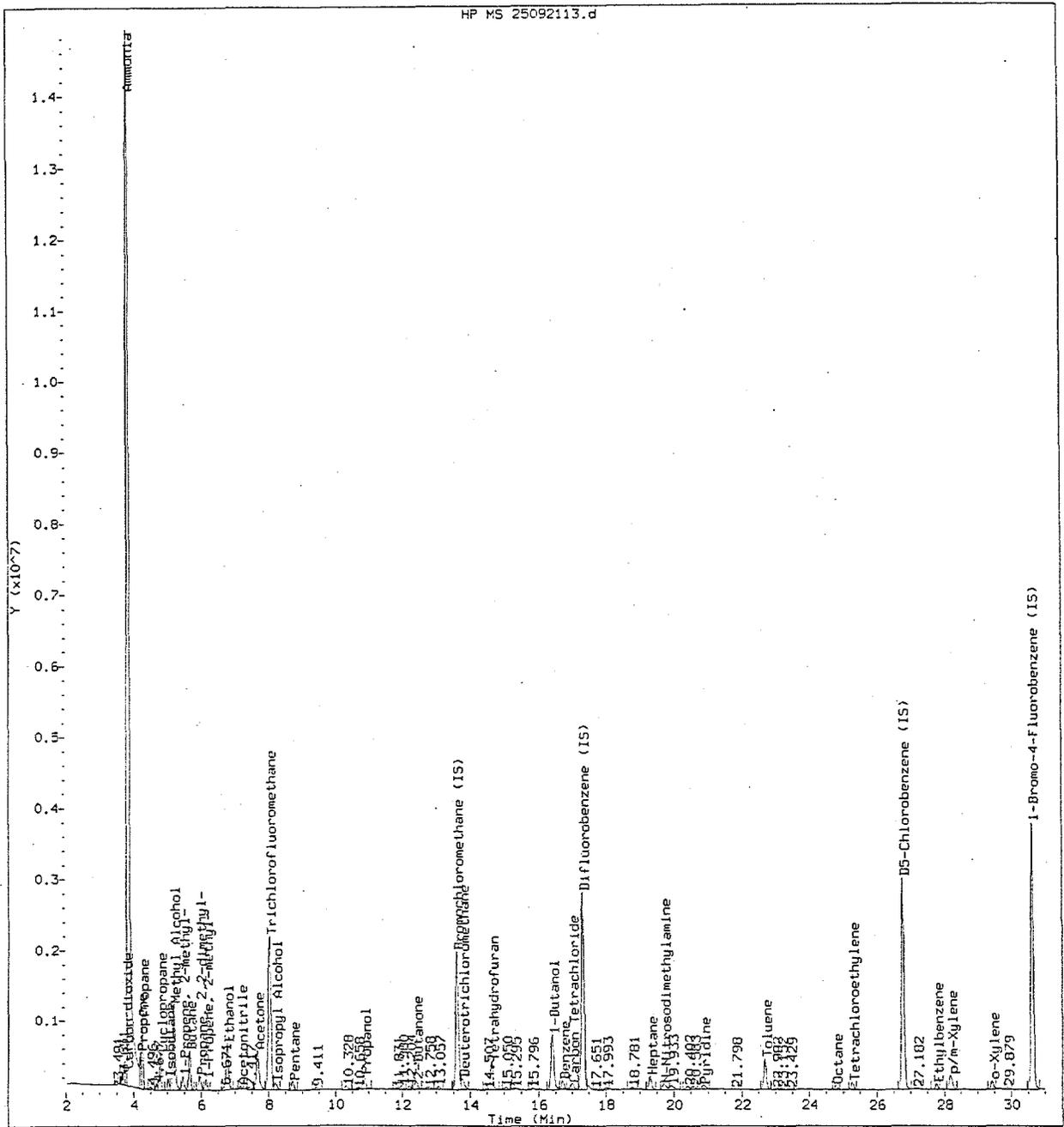


Figure D.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank U-109 SUMMA™ Canister Sample S5055-A04-252 Collected on 8/10/95

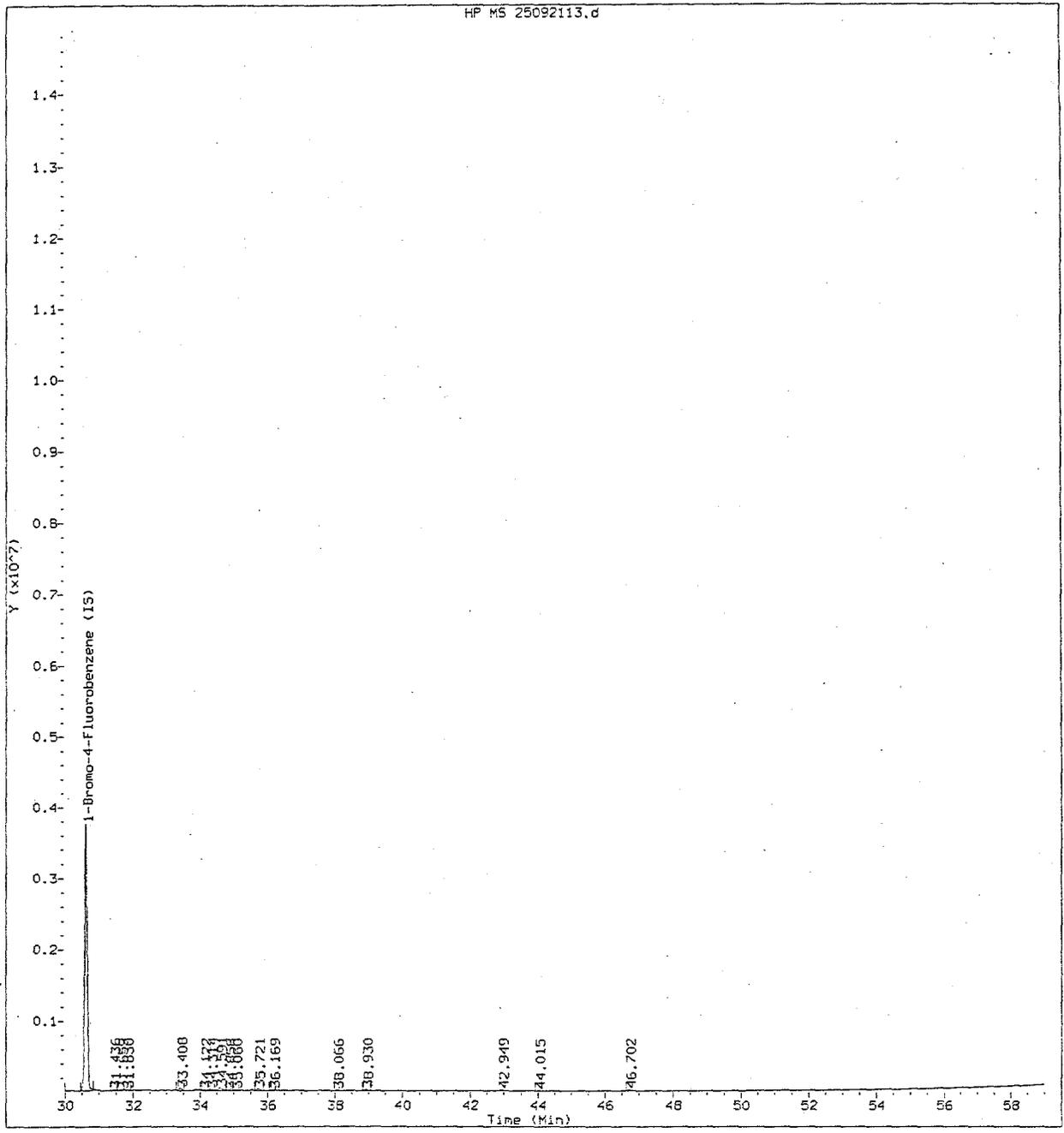
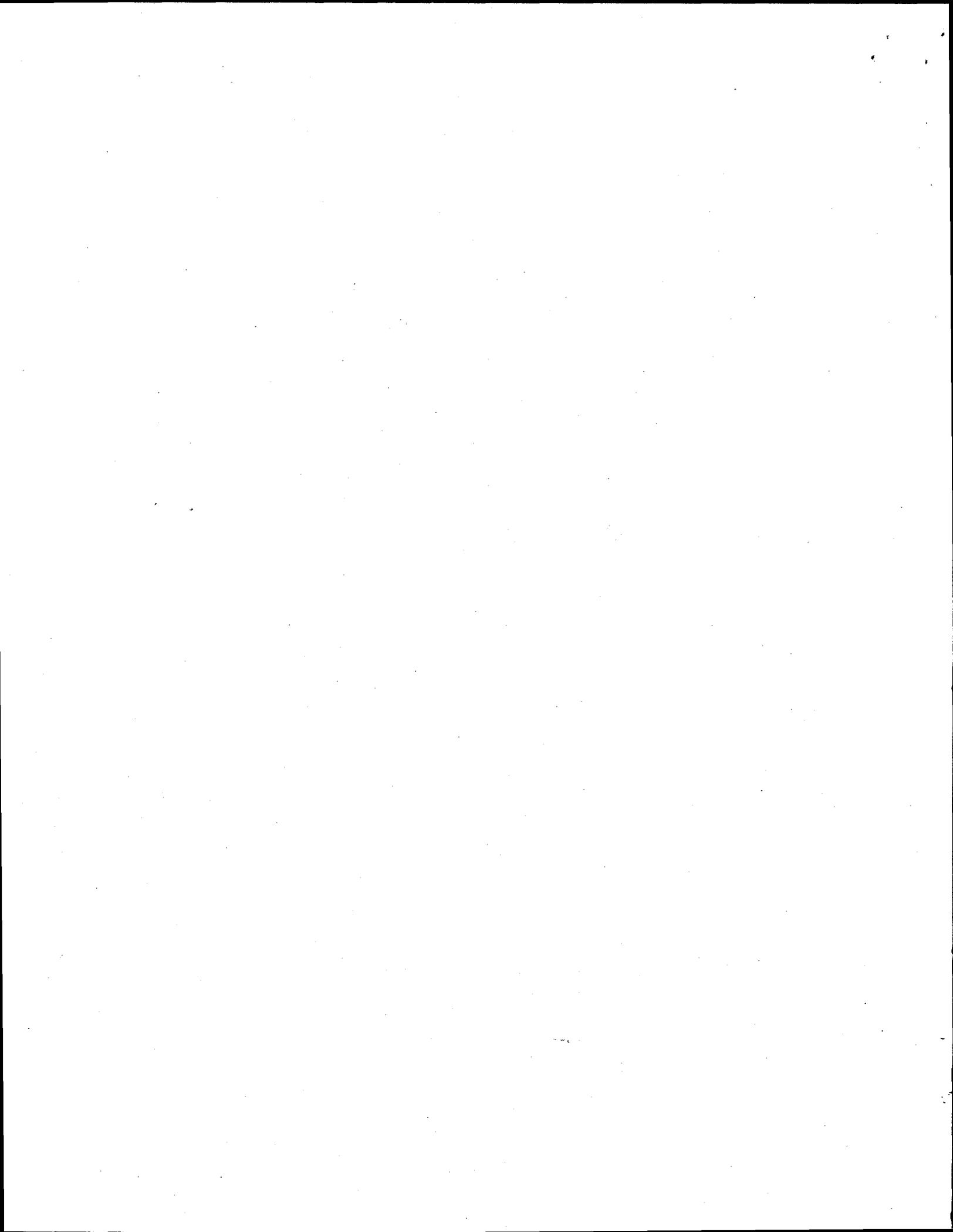
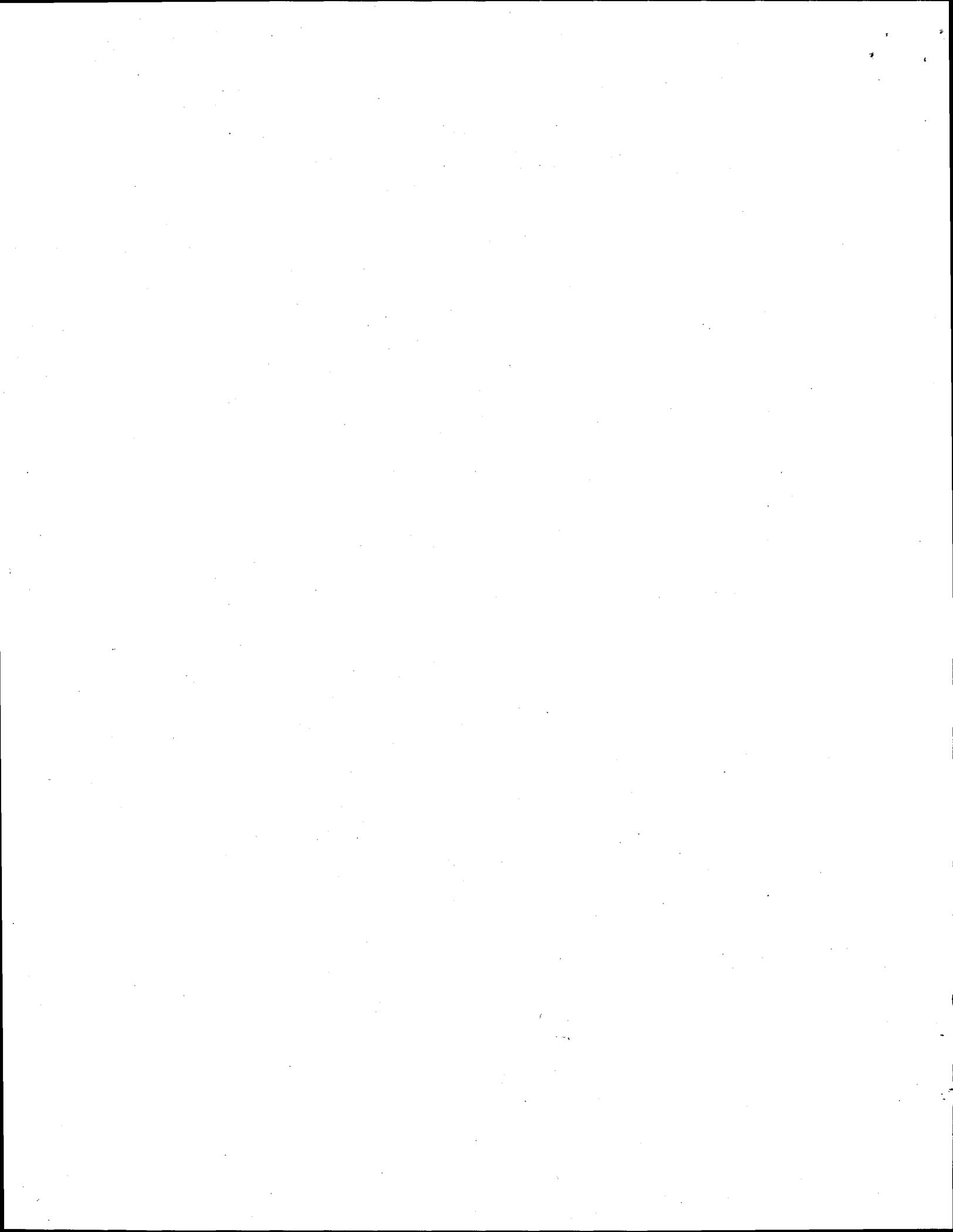


Figure D.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank U-109
SUMMA™ Canister Sample S5055-A04-252 Collected on 8/10/95



Appendix E

Tank Vapor Characterization: Semi-Volatile Organic Analytes



Appendix E

Tank Vapor Characterization: Semi-Volatile Organic Analytes

E.1 Sampling Methodology

Samples are collected on Supelco 300 graphite-based triple sorbent traps (TSTs). Before field deployment, each trap is heated to 380°C under inert gas flow for a minimum of 60 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 three surrogate compounds (hexafluorobenzene, toluene-d8, and bromobenzene-d5). One per batch tube is run immediately to verify successful addition of surrogate spikes to that batch. Tubes are then placed in individually labeled plastic shipping tubes (Supelco TD³), which are sealed with gasketed end caps, thus providing a rugged, headspace-free shipping and storage medium. As a precautionary measure, sample tubes are kept in refrigerated storage before and after sampling.

E.2 Analytical Procedure

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

(a) Pacific Northwest Laboratory. 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.

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

The instrument calibration mixture for the TST analysis consists of 60 compounds. These 60 compounds that are directly quantified in this analysis make up the target analyte list (these 60 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table E.1. The standard calibration mix was analyzed using four aliquot sizes ranging from 100 mL to 1200 mL, and a response factor for each compound was calculated. Volumes of standard added to the traps are measured by pressure difference on a SUMMA™ canister of known volume. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. Performance-based detection limits for the target analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 parts per billion by volume (ppbv) is used.

Table E.1. Target Organic Analytes

<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
1,1-Dichloroethane	1,2,4-Trichlorobenzene	cis-1,2-Dichloroethene
Hexachloro-1,3-butadiene	Chloroform	2-Butanone
1,2-Dichloroethane	<i>Acetone</i>	1,1,2-Trichloroethane
<i>Acetonitrile</i>	Benzene	Heptane
Carbon Tetrachloride	Tetrahydrofuran	1,2-Dichloropropane
Pyridine	Trichloroethene	Butanenitrile
Undecane	Cyclohexane	trans-1,3-Dichloropropene
Decane	1,1,1-Trichloroethane	Hexane
Toluene	4-Methyl-2-pentanone	1,2-Dibromoethane
Propanenitrile	Tetrachloroethylene	Cyclohexanone
Ethylbenzene	Propanol	p-Xylene
Chlorobenzene	Butane	Pentane
1-Butanol	Octane	Nonane
Dodecane	Tridecane	Tetradecane
1,4-Dichlorobenzene	1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichlorobenzene

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

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

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

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

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

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

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

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

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

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

E.4 Semi-Volatile Organic Sample Results

Ten TSTs consisting of six samples, two field blanks, and two trip blanks were returned to the laboratory on August 14, 1995, under WHC chain-of-custody 009252. The samples were analyzed on September 25 and 26, 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. Twenty target analytes above the 5-ppbv reporting cutoff and 11 TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. Nineteen of 20 target analytes and 9 of 11 TICs were observed in two or more sorbent traps. Two of 11 TICs were identified as unknowns. Trichlorofluoromethane, (2.03 mg/m^3), 1-butanol (1.02 mg/m^3), and acetone (0.64 mg/m^3) accounted for 61% of the target analytes and 34% of the total concentration identified by both the target and TIC analyses. The total concentration of the target analytes was found to be 6.07 mg/m^3 or 56% of the total concentration identified by both the target and TIC analyses. The predominant TICs observed in these samples were 1-chloro-1,1-difluoroethane (3.27 mg/m^3), ethanol (0.89 mg/m^3), and n-nitrosodimethylamine (0.23 mg/m^3), which accounted for 91% of the TICs and 40% of the total concentration identified by both the target and TIC analyses. The total concentration of the TICs was found to be 4.84 mg/m^3 or 44% of the total concentration identified by both the target and TIC analyses. The total concentration of all the compounds identified was 10.91 mg/m^3 .

Triple sorbent trap sample PNL 649 was analyzed in replicate for target analytes and TICs to determine analytical precision. The relative percent difference (RPD) results are presented in Table E.3. The RPD was calculated for analytes detected above the detection limit and found in both replicates. Seventeen of 20 target analytes and 4 of 9 TICs had RPDs of less than 10%.

This run proceeded without incident. The IS checks were satisfactory according to currently accepted criteria ($\pm 50\%$ relative to initial continuing calibration verification [CCV]) for all samples. Several of the blanks had ISs which differed from the initial CCV by slightly more than the criteria stated in TVP-10 Rev 0 (30%). Internal standard reproducibility on the tank samples was excellent. The field and trip blanks were clean of target compounds except for a trace of methylene chloride in the first field blank. All four field and trip blanks contained varying amounts of an early eluting TIC tentatively identified as 1-chloro-1,1-difluoroethane. That compound was also present in all three of the tank samples (and repeat) at exceptionally high levels. It probably represents an erratic storage artifact. The CCV checks were generally satisfactory for most compounds in all three CCVs. Specific exceptions included: CCV-1, chloromethane, tridecane, and tetradecane; CCV-2, no exceptions; CCV-3, chloromethane, 1,2-dichloro-1,1,2,2-tetrafluoroethane, and decane. Lab blanks

were clean. The surrogate recoveries were within method limits for all three of the tank samples and three of the blanks. Trip blank #1 had an unacceptably low surrogate recovery. Target compounds found in one or more samples at significant levels included butane, acetonitrile, acetone, trichlorofluoromethane, pentane, methylene chloride, propanol, 2-butanone, hexane, tetrahydrofuran, 1-butanol, benzene, heptane, 4-methyl-2-pentanone, toluene, tetrachloroethene, p+m-xylene, o-xylene, with trace amounts of several other target compounds. A number of TICs were observed including propene, methyl alcohol, ethanol, 2-methyl-2-propanol, 2,2-dimethyl-butane, n-nitrosodimethylamine, pyrazine, and minor amounts of several other compounds. The first sample continued to show a very large tributyl phosphate peak with a smaller dibutyl butanephosphonate peak. Those peaks were completely absent from the other two samples and repeat. This pattern has been present in all tanks sampled with TSTs after Tank AX-103.

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

1. The standard calibration mix was analyzed using four aliquot sizes ranging from 100 mL to 1200 mL. This varies from PNL-TVP-10 because a 30-mL aliquot size was not analyzed.
2. 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.
3. The surrogates were added to each sample tube before going to the field, and they were analyzed in conjunction with each sample except the system blank. The surrogates were not added to the "Lab Blanks."
4. Procedure PNL-TVP-10 states that four ISs are used for quantification. One of those standards, bromochloromethane, was removed from the method before analysis of the tank samples. Bromochloromethane has been found to exhibit unacceptably erratic behavior as an IS for the TST method. The next revision of 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 U-109 on 8/10/95.

Target Analytes ^(a)	CAS No.	Mol Wt	Ret Time	S5055-A13.651 ^(c)		S5055-A06.649 ^{(c)(d)}		S5055-A07.650 ^(e)		Mean and Standard Deviations ^(b)		
				PNL 651 ^(e) (mg/m ³) (ppbv)	PNL 649 ^{(c)(d)} (mg/m ³) (ppbv)	PNL 650 ^(e) (mg/m ³) (ppbv)	PNL 650 ^(e) (mg/m ³) (ppbv)	(mg/m ³)	St.Dev (ppbv)	St.Dev		
Acetonitrile	75-05-8	41.1	38	0.07	0.07	38	0.09	47	0.08	0.01	41	5.3
Acetone	67-64-1	58.1	242	0.63	0.65	249	0.65	252	0.64	0.01	248	5.0
Trichlorofluoromethane	75-69-4	137.4	328	2.01	1.97	321	2.10	342	2.03	0.07	330	10.7
Methylene Chloride	75-09-2	84.9	13	0.05	0.49	128	0.25	66	0.26	0.22	69	57.5
Propanol	71-23-8	60.1	252	0.68	0.62	231	0.67	249	0.66	0.03	244	11.2
2-Butanone	78-93-3	72.1	24	0.08	0.08	25	0.08	24	0.08	0.00	24	0.9
Hexane	110-54-3	86.2	19	0.07	0.07	19	0.08	20	0.07	0.01	19	0.3
Tetrahydrofuran	109-99-9	72.1	91	0.29	0.28	87	0.27	85	0.28	0.01	87	3.3
Benzene	71-43-2	78.1	14	0.05	0.05	14	0.05	14	0.05	0.00	14	0.2
Trichloroethene	79-01-6	131.4	<5	<0.03	0.03	6	<0.03	<5	(g)	(g)	(g)	(g)
Heptane	142-82-5	100.2	10	0.04	0.04	10	0.04	10	0.04	0.00	10	0.0
4-Methyl-2-Pentanone	108-10-1	100.2	9	0.04	0.04	9	<0.02	<5	0.04	(g)	9	(g)
Toluene	108-88-3	92.1	39	0.16	0.17	41	0.17	41	0.17	0.01	40	1.5
Tetrachloroethylene	127-18-4	165.8	5	0.04	0.04	5	0.04	6	0.04	0.00	5	0.2
Ethylbenzene	100-41-4	106.2	6	0.03	0.03	7	0.03	7	0.03	0.00	7	0.3
p/m-Xylene ^(g)	106-42-3	106.2	24	0.11	0.12	25	0.12	26	0.12	0.01	25	0.7
o-Xylene	95-47-6	106.2	11	0.05	0.05	12	0.06	12	0.05	0.01	12	0.4
Butane	106-97-8	58.14	110	0.29	0.31	118	0.34	129	0.31	0.03	119	9.5
Pentane	109-66-0	72	33	0.10	0.09	30	0.10	32	0.10	0.01	31	1.6
1-Butanol	71-36-3	74	312	1.03	0.97	293	1.05	317	1.02	0.04	307	12.3
Tentatively Identified Compound^(b)												
Propene	115-07-1	42	79	0.148	0.131	70	0.194	103	0.16	0.03	84	17.4
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	124	0.554	5.744	1287	3.517	788	3.27	2.60	733	583
Methyl Alcohol	67-56-1	32	733	1.047	<0.01	<10	<0.01	<10	(g)	(g)	(g)	(g)
Ethanol	64-17-5	46	398	0.818	0.880	429	0.961	468	0.89	0.07	432	34.9
2-Propanol, 2-methyl-	75-65-0	74	<10	<0.03	0.087	26	0.088	27	0.09	(g)	26	(g)
Butane, 2,2-dimethyl-	75-83-2	86	10	0.039	0.052	14	0.057	15	0.05	0.01	13	2.4
Unknown			(h)	0.027	0.014	(h)	0.031	(h)	0.02	0.01	(g)	(g)
N-Nitrosodimethylamine	62-75-9	74	74	0.246	0.210	64	0.232	70	0.23	0.02	69.4	5.5

U-109 Table E.2 (Contd)

Tentatively Identified Compound ^(a)	CAS No.	Mol Wt	Ret Time	S5055-A13.651 ^(c)		S5055-A06.649 ^{(d)(e)}		S5055-A07.650 ^(c)		Mean and Standard Deviations ^(f)			
				PNL 651 ^(c)	(mg/m ³) (ppbv)	PNL 649 ^{(d)(e)}	(mg/m ³) (ppbv)	PNL 650 ^(c)	(mg/m ³) (ppbv)	St Dev	St Dev	(mg/m ³) (ppbv)	St Dev
Pyrazine	290-37-9	80	21.9	0.094	26	0.076	21	0.091	25	0.09	0.01	24.4	2.7
Unknown			27.8	0.041	(h)	0.046	(h)	0.045	(h)	0.04	0.00	(g)	(g)
Phosphoric acid tributyl ester	126-73-8	266	59.3	0.118	10	<0.12	<10	<0.12	<10	(g)	(g)	(g)	(g)

(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 and WILEY Libraries.

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

(h) Molecular weight not available

(i) Mean and standard deviations based on analytical values reported to two or three decimal places, not face values reported in table.

(j) Target analyte ppb values reported to two decimal places, but rounded to the whole integer in individual TST results.

(k) m-Xylene and p-Xylene coelute; the reported concentration is the sum of these two compounds.

Table E.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b)
 Results of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank U-109 on 8/10/95

Target Analytes	CAS No.	Mol Wt	Ret Time	S5055-A06.649 ^(c)		S5055-A06.649 ^(c)		Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	
Acetonitrile	75-05-8	41.1		0.07	38	0.07	41	0
Acetone	67-64-1	58.1		0.65	249	0.63	244	3
Trichlorofluoromethane	75-69-4	137.4		1.97	321	1.95	317	1
Methylene Chloride	75-09-2	84.9		0.49	128	0.48	127	2
Propanol	71-23-8	60.1		0.62	231	0.53	199	16
2-Butanone	78-93-3	72.1		0.08	25	0.08	25	0
Hexane	110-54-3	86.2		0.07	19	0.07	19	0
Tetrahydrofuran	109-99-9	72.1		0.28	87	0.28	86	0
Benzene	71-43-2	78.1		0.05	14	0.05	14	0
Trichloroethene	79-01-6	131.4		0.03	6	0.03	6	0
Heptane	142-82-5	100.2		0.04	10	0.04	9	0
4-Methyl-2-Pentanone	108-10-1	100.2		0.04	9	0.04	9	0
Toluene	108-88-3	92.1		0.17	41	0.17	41	0
Tetrachloroethylene	127-18-4	165.8		0.04	5	0.04	5	0
Ethylbenzene	100-41-4	106.2		0.03	7	0.03	7	0
p/m-Xylene	106-42-3	106.2		0.12	25	0.12	25	0
o-Xylene	95-47-6	106.2		0.05	12	0.06	12	18
Butane	106-97-8	58.14		0.31	118	0.31	118	0
Pentane	109-66-0	72		0.09	30	0.11	33	20
1-Butanol	71-36-3	74		0.97	293	0.98	297	1
Tentatively Identified Compound^(e)								
Propene	115-07-1	42	5.9	0.131	70	0.112	60	16
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	6.4	5.744	1287	5.799	1299	1
Methyl Alcohol	67-56-1	32	6.7	<0.01	<10	<0.01	<10	2
Ethanol	64-17-5	46	8.4	0.880	429	0.865	421	20
2-Propanol, 2-methyl-	75-65-0	74	11.0	0.087	26	0.071	21	24
Butane, 2,2-dimethyl-	75-83-2	86	12.3	0.052	14	0.041	11	76
Unknown			20.1	0.014	(f)	0.031	(f)	5
N-Nitrosodimethylamine	62-75-9	74	21.6	0.210	64	0.221	67	18
Pyrazine	290-37-9	80	21.9	0.076	21	0.091	25	

U-109 Table E.3 (Contd)

Tentatively Identified Compound ^(a)	CAS No.	Mol Wt	Ret Time	S5055-A06.649 ^(c)		S5055-A06.649 ^(e)		Relative Percent Difference ^(g)
				PNL 649 ^(d) (mg/m ³)	(ppbv)	PNL 649 ^(d) (mg/m ³)	(ppbv)	
Unknown			27.8	0.046	(f)	0.045	(f)	2
Phosphoric acid tributyl ester	126-73-8	266	59.3	<0.12	<10	<0.12	<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 and WILEY Libraries.
- (f) No molecular weight available for calculation.
- (g) Relative percent differences (RPDs) based on mg/m³ values; target analyte RPDs based on analytical values reported to two decimal places; TIC RPDs are based on analytical values reported to three decimal places.

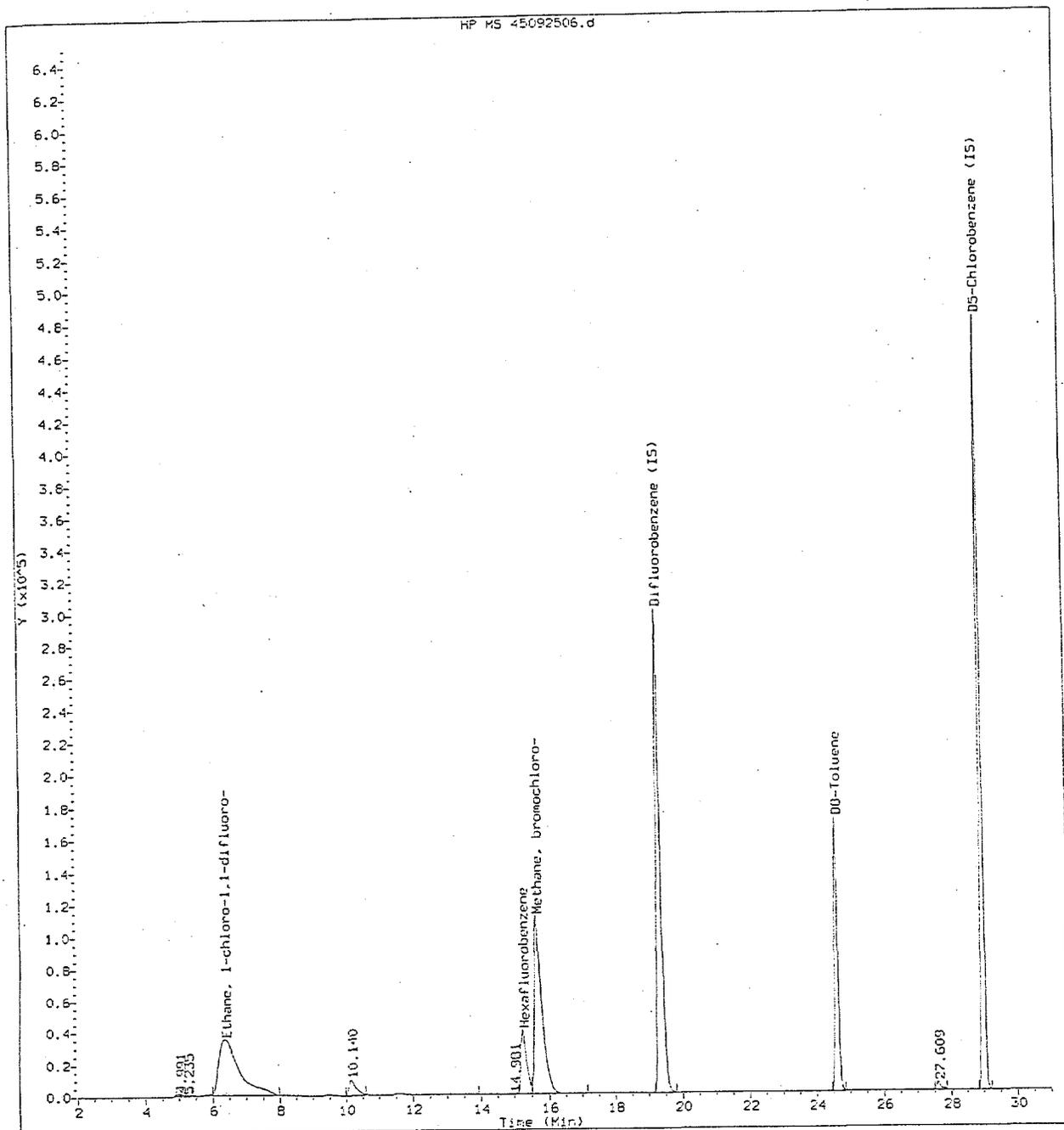


Figure E.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank U-109 Triple Sorbent Trap Sample S5055-A23-656 Collected on 8/10/95

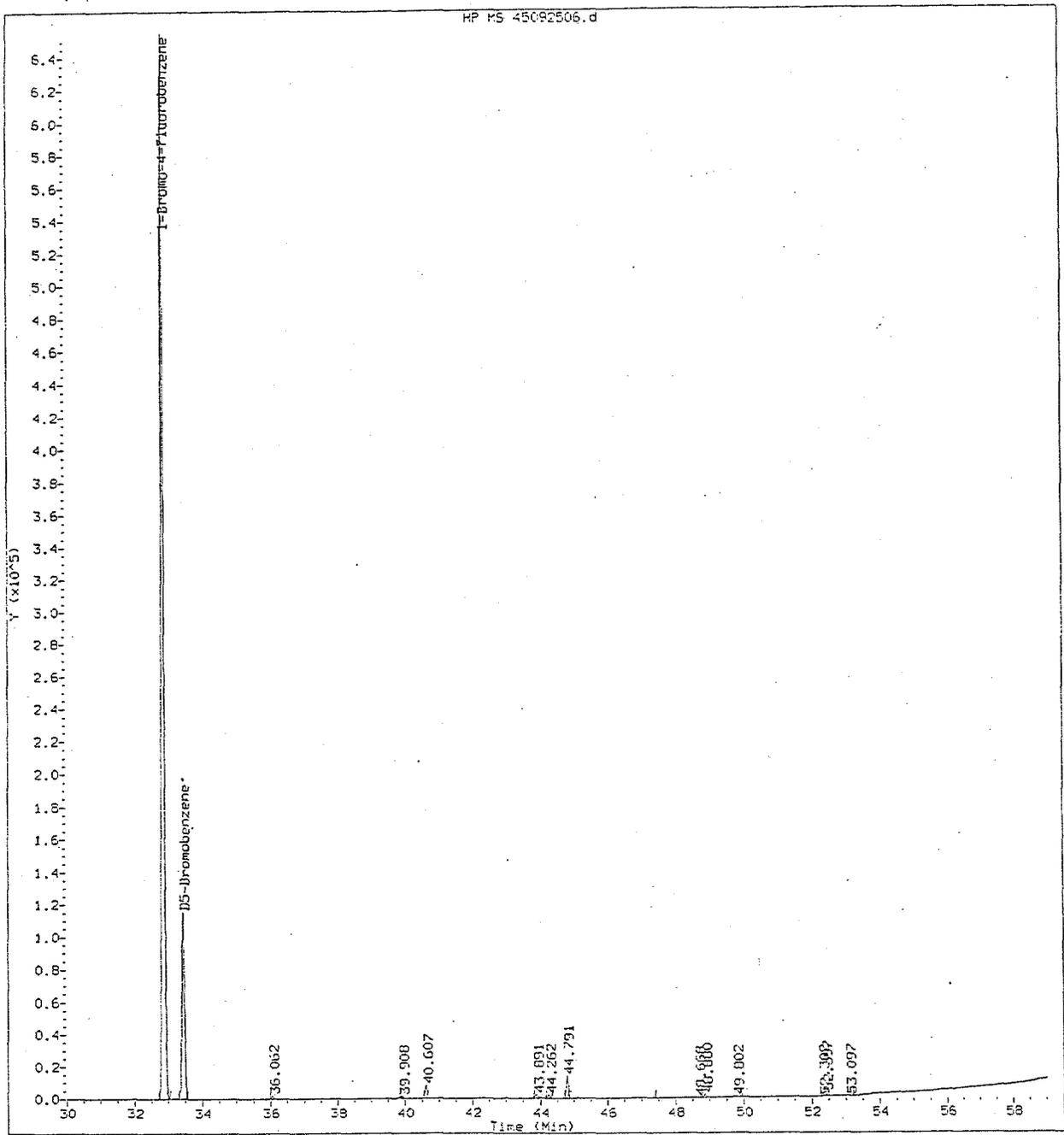
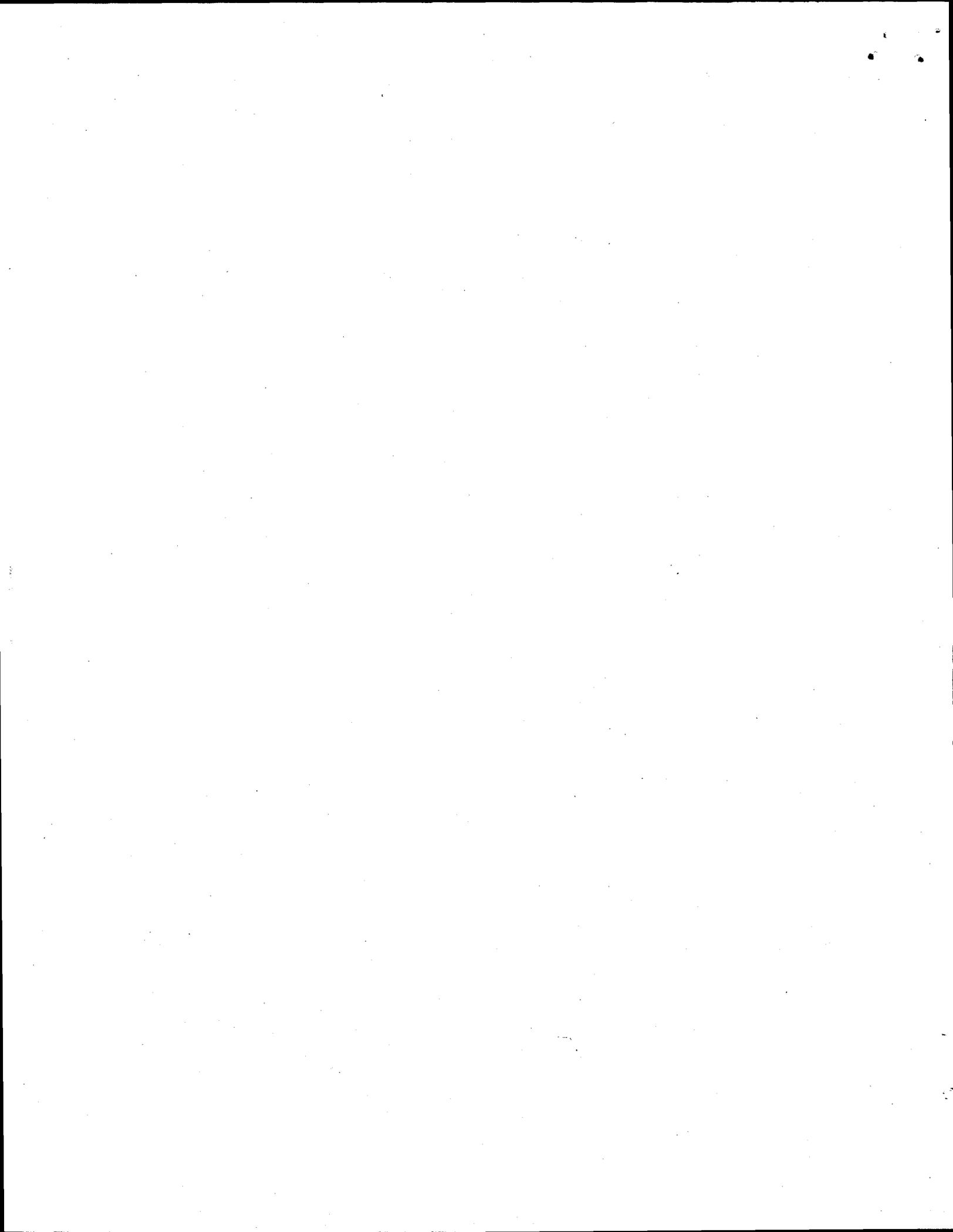


Figure E.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank U-109 Triple Sorbent Trap Sample S5055-A23-656 Collected on 8/10/95



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-U-109 Tank Vapor Sample SAF S5055
(VSS Truck)

Collection date 08 - 10 - 95
Preparation date 08 - 09 - 95

Ice Chest No.

Field Logbook No. WHC-N-647-10

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to WHC

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S5055 - A08 . 77T	NH ₃ /NO _x /H ₂ O	(INORG Sorbent Trap # 1)
S5055 - A09 . 78T	NH ₃ /NO _x /H ₂ O	(INORG Sorbent Trap # 2)
S5055 - A10 . 79T	NO _x /H ₂ O	(INORG Sorbent Trap # 3)
S5055 - A11 . 80T	NH ₃ /H ₂ O/H ₂ O	(INORG Sorbent Trap # 4)
S5055 - A16 . 81T	NH ₃ /NO _x /H ₂ O	(INORG Sorbent Trap # 5)
S5055 - A17 . 82T	NH ₃ /NO _x /H ₂ O	(INORG Sorbent Trap # 6)
S5055 - A18 . 83T	NO _x /H ₂ O	(INORG Sorbent Trap # 7)
S5055 - A19 . 84T	NH ₃ /H ₂ O/H ₂ O	(INORG Sorbent Trap # 8)
S5055 - A25 . 85T	NH ₃ /NO _x /H ₂ O	(INORG Field Blank # 1)
S5055 - A26 . 86T	NH ₃ /NO _x /H ₂ O	(INORG Field Blank # 2)
S5055 - A27 . 87T	NH ₃ /NO _x /H ₂ O	(INORG Field Blank # 3)

[] Field Transfer of Custody		[] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
G W Dennis <i>G.W. Dennis</i>	08-09-95	1445	J A Edwards <i>J A Edwards</i>	08-09-95	1445
J A Edwards <i>J A Edwards</i>	08-09-95	1445	T.B. Utter <i>T.B. Utter</i>	08-09-95	1445
T.B. Utter <i>T.B. Utter</i>	8-14-95	0930	J A Edwards <i>J A Edwards</i>	08-14-95	0930
J A Edwards <i>J A Edwards</i>	8-15-95	1400	G.W. Dennis <i>G.W. Dennis</i>	8-15-95	1400
G.W. Dennis <i>G.W. Dennis</i>	8-16-95	1515	K.H. Pool <i>K.H. Pool</i>	8-16-95	1515

Final Sample Disposition

Comments:

PNL (only) Checklist	Pick-up / Delivery	Comments:
Media labeled and checked?	(Y) N	
Letter of instruction?	(Y) N	
Media in good condition?	(Y) N	
COC info/signatures complete?	(Y) N	
Sorbents shipped on ice? (<10°C)	(Y) N	
Rad release stickers on samples?	(Y) N	
Activity report from 222S?	(Y) N	
COC copy for LRB, RIDS filed?	(Y) N	
COC copy for sorbent follow-on?	(Y) N	
	POC (Y) N	Original COC follows sorbent media

Battelle
Pacific Northwest Lab

CHAIN OF CUSTODY

WHC 009251

Custody Form Initiator J. A. Edwards - PNL

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

Company Contact R. D. Mahon - WHC

Telephone (509) 373-2891
Page 85-3152 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm
241-U-109 Tank Vapor Sample SAF S5055
(VSS Truck)

Collection date 08 - 10 - 95
Preparation date 08 - 09 - 95

Ice Chest No.

Field Logbook No. WHC- N-617-10

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to PNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S5055 - A01 . 213 Ambient Air SUMMA #1 Upwind of U-109
S5055 - A02 . 251 Ambient Air SUMMA #2 Through Port # 15

S5055 - A04 . 252 SUMMA #3 Port # 15
S5055 - A12 . 254 SUMMA #4 Port # 15
S5055 - A20 . 255 SUMMA #5 Port # 13

[] Field Transfer of Custody		[] Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
J A Edwards <i>J Edwards</i>	08-09-95	1415	T.B. UTEH <i>T.B. UTEH</i>	08-09-95	1415	
T.B. UTEH <i>T.B. UTEH</i>	8-14-95	0915	J A Edwards <i>J Edwards</i>	8-14-95	0915	

Final Sample Disposition

Comments:

- | PNL (only) Checklist | Pick-up / Delivery | Comments: |
|---|---|-----------------|
| <input type="checkbox"/> Media labeled and checked? | <input checked="" type="checkbox"/> Y / N | |
| <input type="checkbox"/> Letter of instruction? | <input checked="" type="checkbox"/> Y / N | |
| <input type="checkbox"/> Media in good condition? | <input checked="" type="checkbox"/> Y / N | |
| <input type="checkbox"/> COC info/signatures complete? | <input checked="" type="checkbox"/> Y / N | |
| <input type="checkbox"/> Rad release stickers on samples? | <input checked="" type="checkbox"/> Y / N | |
| <input type="checkbox"/> Activity report from 222S? | <input checked="" type="checkbox"/> Y / N | |
| <input type="checkbox"/> COC copy for LRB, RIDS filed? | <input checked="" type="checkbox"/> Y / N | |
| | POC <i>(18)</i> | POC <i>(18)</i> |

(Revised 10/17/94 PNL)

Custody Form Initiator J. A. Edwards - PNL Telephone (509) 373-0141
Page 85-3009 / PB-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 Collection date 08 - 10 - 95
241-U-109 Tank Vapor Sample SAF S5055 Preparation date 08 - 01 - 95
(VSS Truck)

Ice Chest No. Field Logbook No. WHC- W-64210

Enco Hi/Lo thermometer No. PNL-T-00 4

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

S5055 - A05 . 648	PNL Triple Sorbent Trap (TST) Sample # 1	
S5055 - A06 . 649	PNL TST Sample # 2	
S5055 - A07 . 650	PNL TST Sample # 3	
S5055 - A13 . 651	PNL TST Sample # 4	
S5055 - A14 . 652	PNL TST Sample # 5	
S5055 - A15 . 653	PNL TST Sample # 6	
S5055 - A21 . 654	Open, close & store PNL TST Field Blank # 1	In VSS truck
S5055 - A22 . 655	Open, close & store PNL TST Field Blank # 2	In VSS truck
S5055 - A23 . 656	Store PNL TST Trip Blank # 1	None
S5055 - A24 . 657	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	08-09-95	1430	T.B. Urecht	08-09-95	1430
T.B. Urecht	8-14-95	0920	J.A. Edwards	8-19-95	0920

Final Sample Disposition

Comments:

- | | | |
|---|--|---|
| <input type="checkbox"/> PNL (only) Checklist | Pick-up / Delivery | Comments: |
| <input type="checkbox"/> Media labeled and checked? | <input checked="" type="checkbox"/> Y / <input type="checkbox"/> N | |
| <input type="checkbox"/> Letter of instruction? | <input checked="" type="checkbox"/> Y / <input type="checkbox"/> N | |
| <input type="checkbox"/> Media in good condition? | <input checked="" type="checkbox"/> Y / <input type="checkbox"/> N | |
| <input type="checkbox"/> COC info/signatures complete? | <input checked="" type="checkbox"/> Y / <input type="checkbox"/> N | |
| <input type="checkbox"/> Sorbents shipped on ice? (<5°C) | <input checked="" type="checkbox"/> Y / <input type="checkbox"/> N | |
| <input type="checkbox"/> Hi/Lo thermometer - <i>Keep upright!</i> | <input checked="" type="checkbox"/> Y / <input type="checkbox"/> N | |
| <input type="checkbox"/> Hi/Lo thermometer | <input type="checkbox"/> Y / <input checked="" type="checkbox"/> N | 1 Hi <u>15</u> °C / Lo <u>-15</u> °C (pick up at PNL to WHC) |
| <input type="checkbox"/> Red release stickers on samples? | <input type="checkbox"/> Y / <input checked="" type="checkbox"/> N | 1 Hi <u>2</u> °C / Lo <u>5</u> °C (delivery at WHC from PNL) |
| <input type="checkbox"/> Activity report from 222S? | <input type="checkbox"/> Y / <input checked="" type="checkbox"/> N | 1 Hi <u> </u> °C / Lo <u> </u> °C (at return to PNL from WHC) |
| <input type="checkbox"/> COC copy for LRB, RIDS filed? | <input type="checkbox"/> Y / <input checked="" type="checkbox"/> N | 1 Hi <u>3</u> °C / Lo <u>3</u> °C (at delivery from WHC to PNL) |

POC (Signature) POC (Signature)

(Revised 06/21/95 PNL)

