

# Pacific Northwest National Laboratory

Operated by Battelle for the  
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## TANK VAPOR CHARACTERIZATION PROJECT

### Headspace Vapor Characterization of Hanford Waste Tank 241-T-110: Results from Samples Collected on 08/31/95

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May 1996

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

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## Summary

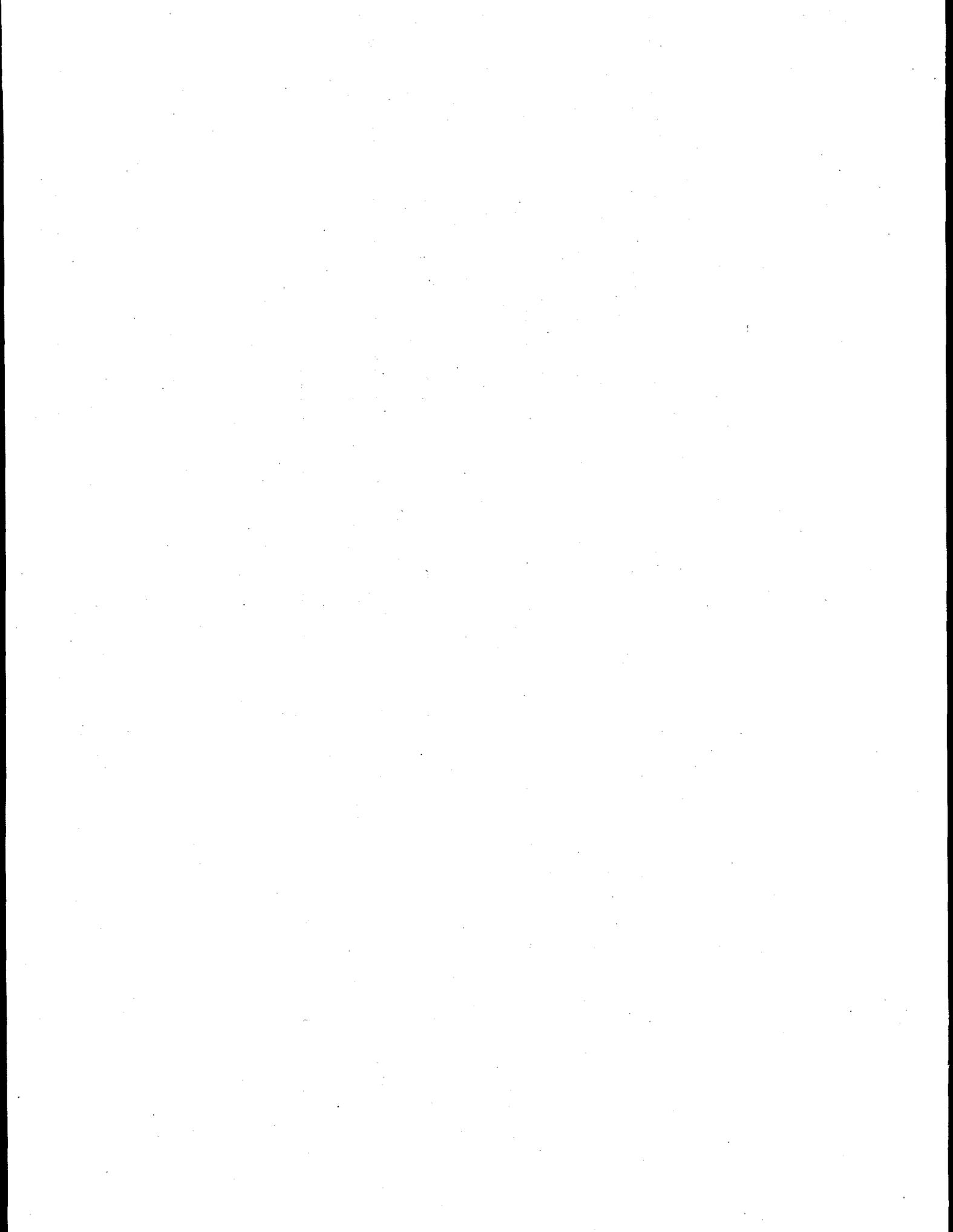
This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-T-110 (Tank T-110) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support safety 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, on 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 the SUMMA™ canister and triple sorbent trap (TST) 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 T-110 on 8/31/95

<u>Category</u>	<u>Sample Medium</u>	<u>Analyte</u>	<u>Vapor<sup>(a)</sup> Concentration</u>	<u>Units</u>
Inorganic Analytes <sup>(b)</sup>	Sorbent Traps	NH <sub>3</sub>	108 ± 1	ppmv
		NO <sub>2</sub>	≤ 0.05	ppmv
		NO	≤ 0.06	ppmv
		H <sub>2</sub> O	16.9 ± 0.2	mg/L
Permanent Gases	SUMMA™ Canister	CO <sub>2</sub>	358	ppmv
		CO	<25	ppmv
		CH <sub>4</sub>	<25	ppmv
		H <sub>2</sub>	<25	ppmv
		N <sub>2</sub> O	<25	ppmv
Total Non-Methane Hydrocarbons (TO-12)	SUMMA™ Canister	Hydrocarbons	1.12	mg/m <sup>3</sup>
Volatile Organics (TO-14)	SUMMA™ Canister	Trichlorofluoromethane	0.007	ppmv
Semi-Volatile Organics (PNL-TVP-10)	Sorbent Traps	Ethane, 1-chloro-1,1-difluoro-	0.101	ppmv
		Methylene Chloride	0.013	ppmv
		Trichlorofluoromethane	0.008	ppmv

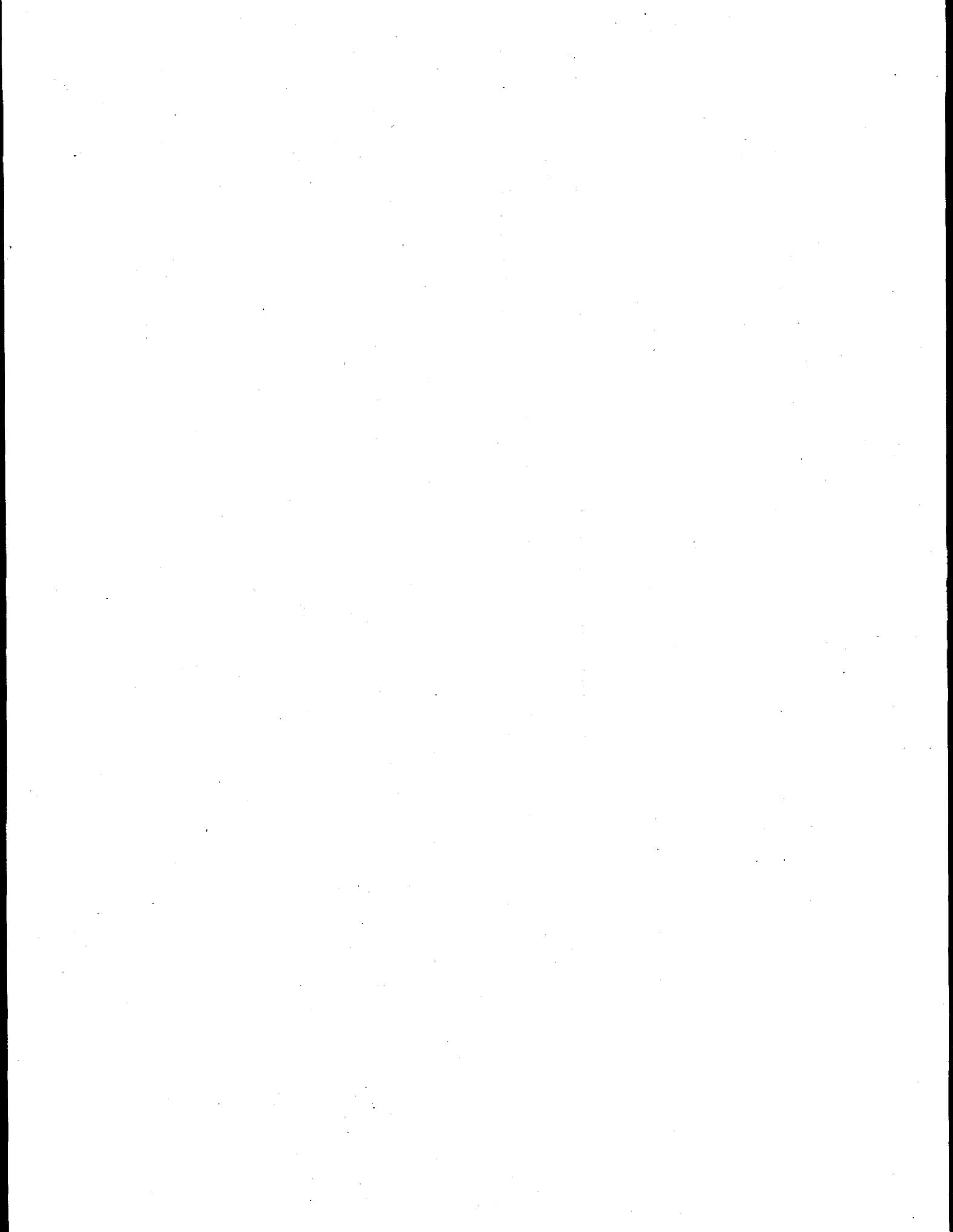
(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data.

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



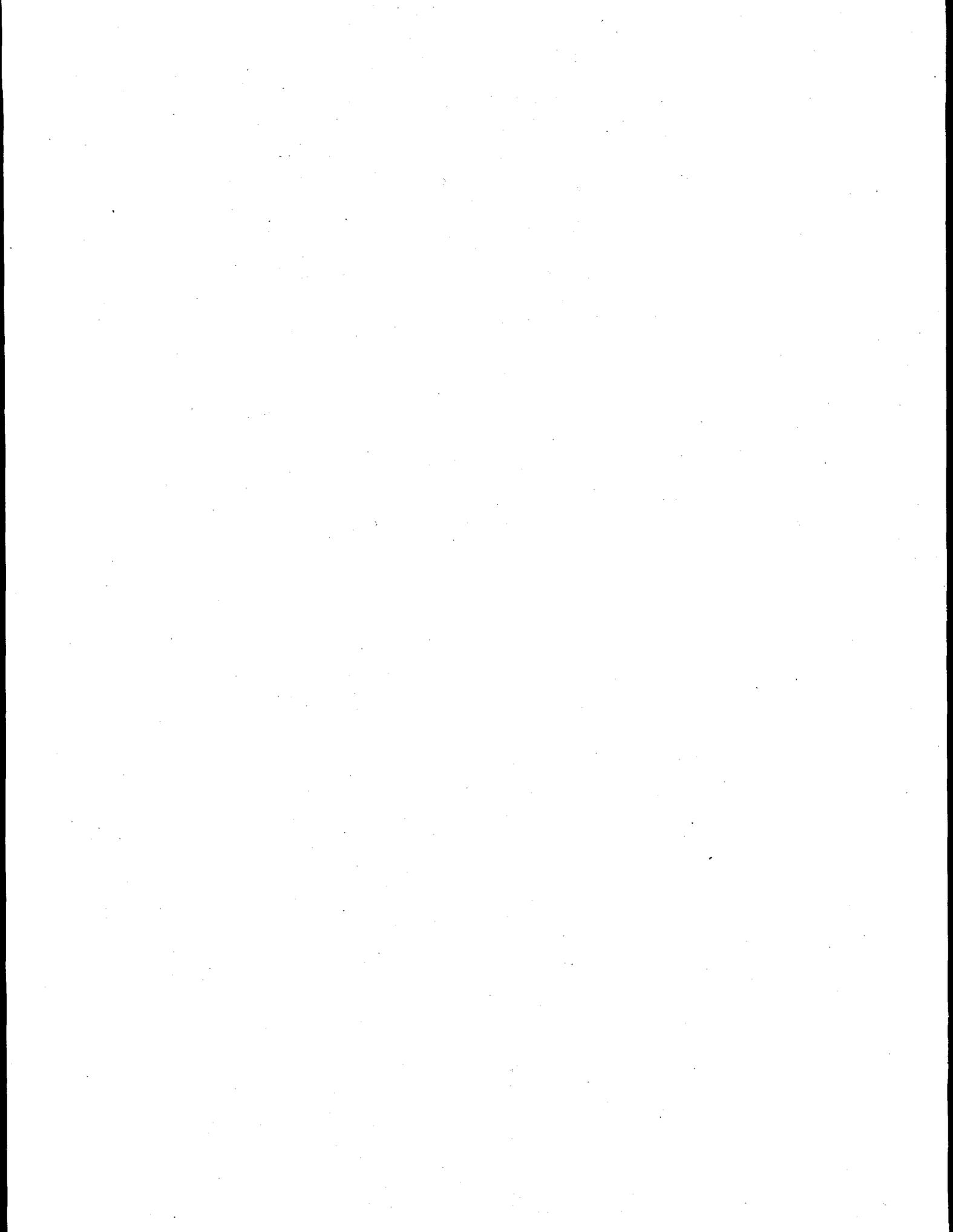
## Acknowledgments

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



## Glossary

CAS	Chemical Abstracts Service
CCV	continuing calibration verification
COC	chain-of-custody
C <sub>v</sub>	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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## 1.0 Introduction

This report describes the results of vapor samples taken from the headspace of waste storage tank 241-T-110 (Tank T-110) at the Hanford Site in Washington State. Pacific Northwest National Laboratory (PNNL)<sup>(a)</sup> 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 S5056. Samples were collected by WHC on August 31, 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 sample 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 and 14, 1995. Exposed samples and controls were returned to PNNL on September 1, 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<sup>(b)</sup>, 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)

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(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.

- *volatile organic analytes* analyses using cryogenic preconcentration followed by gas chromatograph/mass spectrometer (GC/MS)
- *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 T-110 on 8/31/95 (Sample Job S5056) 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  $\text{NH}_3$ ,  $\text{NO}_2$ ,  $\text{NO}$  and vapor mass concentration (primarily  $\text{H}_2\text{O}$ ), were determined. The average and one standard deviation of concentration results from inorganic sorbent sample trains used to sample headspace vapors were  $108 \pm 1$  ppmv ( $\text{NH}_3$ ),  $\leq 0.05$  ppmv ( $\text{NO}_2$ ),  $\leq 0.06$  ppmv ( $\text{NO}$ ), and  $16.9 \pm 0.2$  mg/L (primarily  $\text{H}_2\text{O}$ ). The vapor concentration results were based on six samples for each compound (eight samples for mass concentration). The  $\text{NO}_2$  and  $\text{NO}$  samples included four samples trailing (downstream of)  $\text{NH}_3$  sorbent traps and two samples unprotected by  $\text{NH}_3$  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 (see Table A.1):  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . The precision of results, based on one standard deviation of all samples, was  $\pm 1\%$  (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 ( $\text{NH}_3$ ) and evaluation of the variability of field blanks ( $\text{H}_2\text{O}$ ). 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, 009256, is included in Appendix F.

### 2.2 Permanent Gases

The complete results of the permanent-gas analysis of Tank T-110 can be found in Appendix B of this report. In summary, carbon dioxide at 358 ppmv was the only permanent gas observed above the method detection limit (MDL) in the tank headspace samples, and carbon dioxide in the headspace samples was at similar concentration observed in the ambient air.

### 2.3 Total Non Methane Hydrocarbons

The complete results of the TO-12 analysis of Tank T-110 can be found in Appendix C of this report. In summary, the average concentration in the three tank headspace samples was  $1.12 \text{ mg/m}^3$ . This compares to  $0.04 \text{ mg/m}^3$  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 T-110 can be found in Appendix D of this report. In summary, four target analytes above the 5-ppbv reporting cutoff and no TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. Only one of the target analytes was identified in two or more tank headspace samples. The total concentration of all the compounds identified was 0.04 mg/m<sup>3</sup>. SUMMA™ canister PNL 73 was analyzed in replicate for target analytes and TICs to determine analytical precision. One of two target analytes had relative percent differences (RPDs) of less than 10%. Traces of acetone and pyridine were identified in the ambient air sample. Acetone was also 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 T-110 can be found in Appendix E of this report. In summary, three target analytes above the 5-ppbv reporting cutoff and two TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. One of two TICs were identified as unknowns. The total concentration of the target analytes was 0.12 mg/m<sup>3</sup>. The total concentration of the TICs was 0.50 mg/m<sup>3</sup>. The total concentration of all the compounds identified was 0.62 mg/m<sup>3</sup>. Triple sorbent trap sample PNL 663 was analyzed in replicate for target analytes and TICs to determine analytical precision. All three target analytes had RPDs of less than 10%. Neither of the TICs had RPDs 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 one target analyte and no TICs that were common to both analyses. Trichlorofluoromethane was higher in the TST than the SUMMA™ samples. In addition, acetone, methylene chloride, and 1-chloro-1,1-difluoroethane were observed in the TST sample but were less than MDLs in the SUMMA samples. The presence of 1-chloro-1,1-difluoroethane may represent a storage artifact associated with emission of a refrigerant from a refrigerator.

Table 2.1. Comparison of Mean Values for Positively Identified and Quantitated Target Analytes<sup>(a)</sup> and Tentatively Identified Compounds and Estimated Concentrations<sup>(b)</sup> for Triple Sorbent Traps and SUMMA<sup>TM</sup> Canister Collected from the Headspace of Tank T-110 on 8/31/95

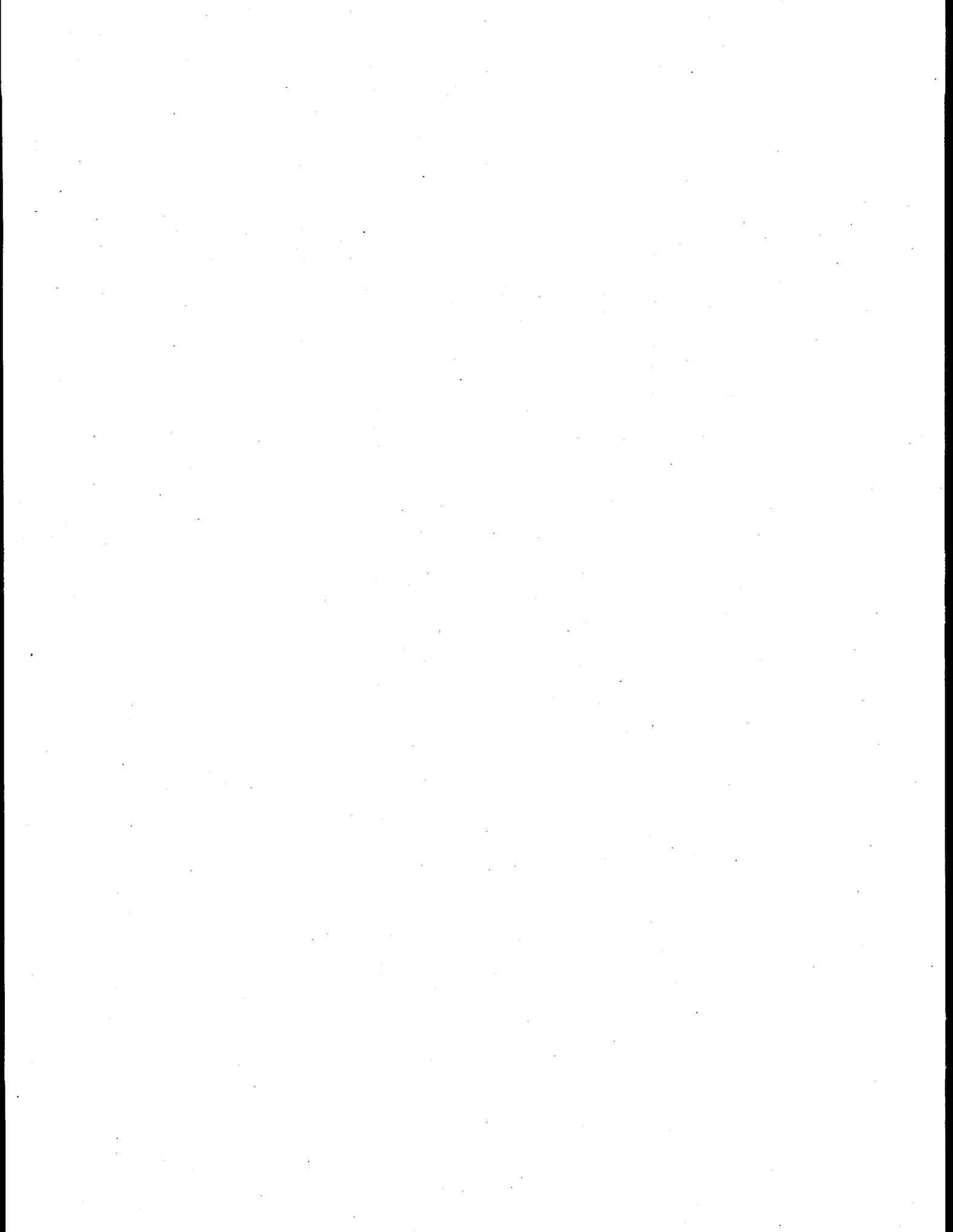
Target Analytes	CAS No.	S5056 <sup>(c)</sup> TST Results		S5056 <sup>(c)</sup> SUMMA <sup>TM</sup> Results		Relative Percent Difference
		(mg/m <sup>3</sup> )	St Dev	(mg/m <sup>3</sup> )	St Dev	
Acetone	67-64-1	0.02	0.00	<0.02		na
Trichlorofluoromethane	75-69-4	0.05	0.00	0.04	0.00	22
Methylene Chloride	75-09-2	0.05	0.03	<0.02		na
<b>Tentatively Identified Compounds<sup>(b)</sup></b>						
Ethane, 1-chloro-1,1-difluoro-	75-68-3	0.45	0.41	<0.04		na

(a) TO-14 plus 22 additional target analytes.

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

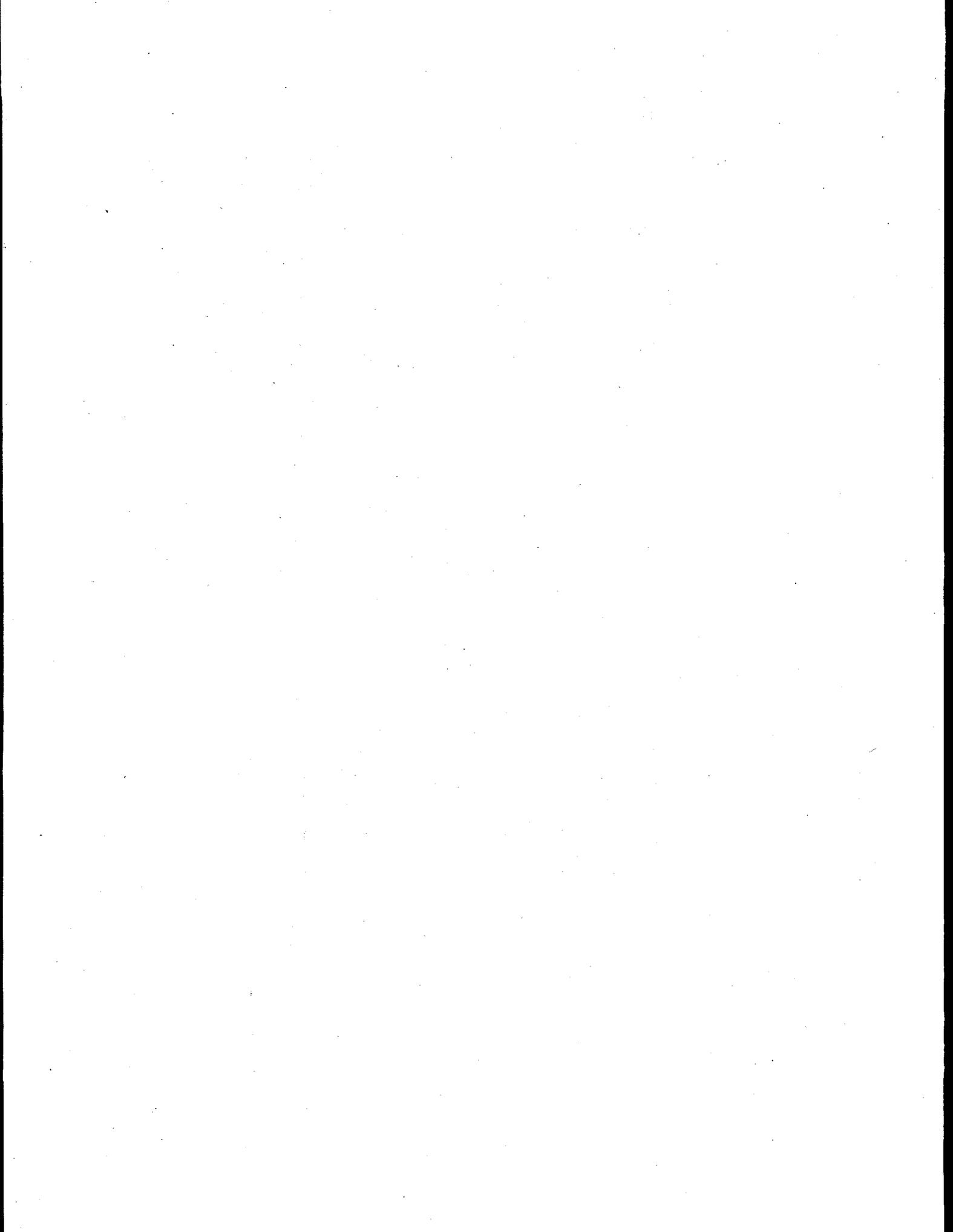
(c) WHC sample job number.

na Not applicable



### 3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank T-110 on August 31, 1995 (Sample Job S5056). The vapor concentrations were based either on whole-volume samples (SUMMA™ canisters) or on sorbent traps exposed to sample flow. In the case of the canisters, the concentrations were based on analytical results and the tracking of dilution/concentration of sample volumes obtained directly from the canisters. In the case of the sorbent traps, concentrations were based on analytical results and sample volumes reported by WHC. Known sampling and analytical variances from established quality assurance requirements, where significant, were documented in this report, as required by the SAP (Homi 1995). No immediate notifications (phone and electronic memo) were provided because analytical results indicated no specific analytes exceeded the notification levels; notification levels and notification procedures are described in the SAP (Homi 1995).



## 4.0 Reference and Further Reading

### Reference

Homi, C. S. 1995. *Vapor Sampling and Analysis Plan*. WHC-SD-WM-TP-335, Rev. OE, Westinghouse Hanford Company, Richland, Washington.

### Further Reading

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

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

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

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

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

## **Appendix A**

### **Tank Vapor Characterization:**

### **Inorganic Analytes**

## Appendix A

### Tank Vapor Characterization: Inorganic Analytes

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to Westinghouse Hanford Company (WHC) for sampling the tank headspace using the Vapor Sampling System (VSS). Blanks, spiked blanks (when requested), and exposed samples were returned to Pacific Northwest National Laboratory (PNNL) for analysis. Analyses were performed to provide information on the tank headspace concentration of the following analytes: ammonia ( $\text{NH}_3$ ), nitrogen dioxide ( $\text{NO}_2$ ), nitric oxide (NO), and water ( $\text{H}_2\text{O}$ ). 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  $\text{NH}_3$  and mass. Samples were prepared, handled, and disassembled as described in Technical Procedure PNL-TVP-09<sup>(a)</sup>. 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  $\text{NH}_3$ , NO,  $\text{NO}_2$ , and  $\text{H}_2\text{O}$  (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  $\text{NH}_3$  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  $\text{NH}_3$  was chemisorbed as ammonium sulfate [ $(\text{NH}_4)_2\text{SO}_4$ ]. The  $\text{NO}_2$  traps contained a zeolite impregnated with triethanolamine (TEA), with 400 mg in the primary and 200 mg in the breakthrough sections. The  $\text{NO}_2$  was absorbed and disproportionated to equi-molar quantities of nitrite ions ( $\text{NO}_2^-$ ) and nitrate ions ( $\text{NO}_3^-$ ). Glass tubes containing 800 mg of an oxidant such as chromate were used to convert NO to  $\text{NO}_2$ . The converted NO was then collected as nitrite and nitrate in an  $\text{NO}_2$  trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sections.

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(a) Pacific Northwest Laboratory. 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<sub>x</sub> 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<sub>v</sub>) of a 3.00-L sample containing 75.0 μg of NH<sub>3</sub> 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  $\text{NH}_3$ -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  $\text{NH}_3$  sorbent traps were analyzed using the selective ion electrode procedure PNL-ALO-226<sup>(a)</sup>. Briefly, this method includes 1) preparing a 1000- $\mu\text{g}/\text{mL}$  (ppm)  $\text{NH}_3$  stock standard solution from dried reagent-grade  $\text{NH}_4\text{Cl}$  and DIW, 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_4\text{Cl}$  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  $\text{NH}_3$  concentration in the samples.

**A.2.2 Nitrite Analysis.** The sorbent traps for  $\text{NO}_2$  and  $\text{NO}$  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<sup>(b)</sup> modified to obviate interferences by concentrations of non-target analytes. Specifically, the modifications used were 1) eluent 1.44 mM  $\text{Na}_2\text{CO}_3$  + 1.8 mM  $\text{NaHCO}_3$  at 2.0 mL/min, 2) one guard column (AG4A) and two separator columns (AS4A) in series instead of just 1 separator column, and 3) all standards, samples, and blanks injected into the IC sample loop through 0.45- $\mu\text{m}$  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  $\text{NO}_2$  and  $\text{NO}$  converted to  $\text{NO}_2$  were collected on the sorbent as equal quantities of nitrite and nitrate, and the analysis was specific for nitrite, the molar masses of  $\text{NO}_2$  and  $\text{NO}$  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  $\text{NH}_3$ ).

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  $\text{NH}_3$  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  $\text{NO}_2$  and  $\text{NO}$ ) 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  $\text{NH}_3$  above, the estimated maximum bias for samples derived from sampling for  $\text{NO}_2$  is  $\pm 10\%$ , and for samples derived from sampling for  $\text{NO}$ , it is  $\pm 5\%$  relative.

**Table A.1 Analytical Procedures, Detection Limits, and Expected and Notification Levels for Selected Inorganic Analytes<sup>(a)</sup>**

Analyte	Formula	Procedure	MDL <sup>(b)</sup> ( $\mu\text{g}$ )	MDL <sup>(b)</sup> (ppmv)	Expected Range <sup>(c)</sup> (ppmv)	Notification Level <sup>(c)</sup> (ppmv)
Ammonia	NH <sub>3</sub>	PNL-ALO-226	0.1	0.5	$\geq 2$	$\geq 150$
Nitrogen Dioxide	NO <sub>2</sub>	PNL-ALO-212	0.02	0.02	$\geq 0.1$	$\geq 10$
Nitric oxide	NO	PNL-ALO-212	0.02	0.02	$\geq 2$	$\geq 50$
Mass (water) <sup>(d)</sup>	n/a	PNL-TVP-09	0.6 mg	0.2 mg/L	$\geq 3$ 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 NH<sub>3</sub> and 3 mL for NO and NO<sub>2</sub>. 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  $\pm 0.1$  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  $\pm 1$  mg per five-trap sorbent train.

#### A.4 Inorganic Sample Results

Samples were obtained by WHC from the tank headspace of Tank T-110 on August 31, 1995 using the VSS. The sample job designation number was S5056. Samples were prepared, submitted to WHC for the sample job, and then returned to PNNL and analyzed to provide information on the concentrations of NH<sub>3</sub>, NO<sub>2</sub>, NO, and mass (primarily H<sub>2</sub>O). Samples were controlled using chain-of-custody 009256 (Appendix F). The inorganic samples were received from WHC on September 1, 1995; the sample volume information was also received on September 1. Analyses were completed on September 7, 1995 (gravimetric, 7-day hold time), September 14, 1995 (ammonia, 14-day hold time), and September 12, 1995 (nitrite, 12-day hold time).

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table A.2. The types of sample trains used and the order of sorbent traps within each train are also shown in the table. For example, the sorbent train NH<sub>3</sub>/NO<sub>x</sub>/H<sub>2</sub>O contained an NH<sub>3</sub> trap at the inlet end, a NO<sub>x</sub> 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  $\text{NH}_3$  was  $108 \pm 1$  ppmv, based on all six samples. The blank-corrected  $\text{NH}_3$  quantities in the sorbent traps ranged from 14.4 to 14.6  $\mu\text{mol}$  in front sections;  $\text{NH}_3$  was not found ( $\leq 0.01 \mu\text{mol}$ ) in back sorbent sections. Blank corrections,  $\leq 0.07 \mu\text{mol}$  in front and  $\leq 0.04 \mu\text{mol}$  in back sections, were about 0.5% 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  $\text{NH}_3$  in the sample and yielded a percentage recovery of 109%. The continuing calibration verification standard, using NIST-traceable material, yielded percentage recoveries of 104 and 108% during the analytical session. A five-point calibration was performed over an  $\text{NH}_3$  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  $\mu\text{mol}$   $\text{NH}_3$  were  $101 \pm 4\%$ ,  $109 \pm 2\%$ , and  $104 \pm 1\%$ , respectively, during previous sample jobs (Clauss et al. 1994; Ligothke et al. 1994).

**A.4.2 Nitrogen Oxides Results.** It is not known whether the presence of an upstream  $\text{NH}_3$  trap typically affects downstream measurements of  $\text{NO}_2$  and  $\text{NO}$ . Consequently, measurements of  $\text{NO}_2$  and  $\text{NO}$  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  $\text{NO}_x$  trains consisted of three segments:  $\text{NO}_2$  trap, oxidizer,  $\text{NO}_2$  trap.) No indication was seen in the present results that  $\text{NO}_2$  or  $\text{NO}$  results differed 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  $\text{NO}_x$  measurements are required. No further evaluation is required of the results from this sample job.

The concentrations of  $\text{NO}_2$  and  $\text{NO}$  were  $\leq 0.05$  and  $\leq 0.06$  ppmv, respectively, based on all six samples. Blank-corrected  $\text{NO}_2^-$  quantities in the sorbent traps averaged  $\leq 0.0030 \mu\text{mol}$  ( $\text{NO}_2$  samples) and  $\leq 0.0040 \mu\text{mol}$  ( $\text{NO}$  samples). Nitrite blank levels used to correct data were  $0.0042 \pm 0.0006 \mu\text{mol}$  in front (three of six blanks analyzed) and  $0.0021 \pm 0.0002 \mu\text{mol}$  in back (two of six blanks analyzed) sorbent sections. The analyses of four samples were duplicated and yielded repeatabilities of  $\pm 1$ ,  $\pm 2$ ,  $\pm 3$ , and  $\pm 1\%$ . Four sample leachates were spiked with 0.25 ppm  $\text{NO}_2^-$  and yielded percentage recoveries of 101, 95, 99, and 94%. 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; Ligothke 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 T-110 on 8/31/95

Sample Number	Sorbent Type	Sample Port and Volume Information <sup>(a)</sup>				
		Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
Samples:						
S5056-A08-88T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O Train	5	200.0	15.0	3.00	0.0552
S5056-A09-89T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O Train	6	200.0	15.0	3.00	0.0547
S5056-A10-90T	NO <sub>x</sub> /H <sub>2</sub> O Train	7	195.6	15.0	2.93	0.0547
S5056-A11-91T	NH <sub>3</sub> /H <sub>2</sub> O/H <sub>2</sub> O Train	8	200.0	15.0	3.00	0.0553
S5056-A16-92T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O Train	5	200.0	15.0	3.00	0.0551
S5056-A17-93T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O Train	6	200.0	15.0	3.00	0.0555
S5056-A18-94T	NO <sub>x</sub> /H <sub>2</sub> O Train	7	194.4	15.0	2.92	0.0548
S5056-A19-95T	NH <sub>3</sub> /H <sub>2</sub> O/H <sub>2</sub> O Train	8	200.0	15.0	3.00	0.0558
Controls:						
S5056-A25-96T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O Field Blank	n/a <sup>(b)</sup>	n/a	n/a	n/a	0.0046
S5056-A26-97T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O Field Blank	n/a	n/a	n/a	n/a	0.0048
S5056-A27-98T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O Field Blank	n/a	n/a	n/a	n/a	0.0051

(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  $16.9 \pm 0.2$  mg/L. The result was based on an average mass gain of 50.3 mg from all eight (NH<sub>3</sub>/NO<sub>x</sub>/H<sub>2</sub>O and NO<sub>x</sub>/H<sub>2</sub>O) sample trains. The blank correction applied to the results was - 4.8 mg per train, based on a mass gain of  $4.8 \pm 0.3$  mg per three five-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of  $\pm 0.1$  mg. Although no spiked blanks were tested, the percentage recovery of mass from three blank H<sub>2</sub>O 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 T-110 on 8/31/95

Sample	Analytical Results ( $\mu\text{mol}$ )			Sample Volume (L)	Vapor <sup>(b)</sup> Concentration (ppmv)
	Front Section	Back Section	Total <sup>(a)</sup> Blank-Corrected		
<u>NH<sub>3</sub> Samples:</u>			<u>14.5<sup>(c)</sup></u>	<u>3.00<sup>(c)</sup></u>	<u>108 ± 1<sup>(c)</sup></u>
S5056-A08-88T	14.6	0.05	14.5	3.00	108
S5056-A09-89T	14.5	NA <sup>(d)</sup>	14.4	3.00	108
S5056-A11-91T	14.6	NA	14.5	3.00	108
S5056-A16-92T	14.7	NA	14.6	3.00	109
S5056-A17-93T	14.5	0.04	14.4	3.00	108
S5056-A19-95T	14.6	NA	14.5	3.00	108
<u>NO<sub>2</sub> Samples:</u>			<u>≤ 0.0030</u>	<u>2.98</u>	<u>≤ 0.05</u>
S5056-A08-88T	0.0059	0.0023	n/a <sup>(d)</sup>	3.00	n/a
S5056-A09-89T	0.0060	NA	n/a	3.00	n/a
S5056-A10-90T <sup>(e)</sup>	0.0062	0.0068 x	n/a	2.93	n/a
S5056-A16-92T	0.0060	0.0020	n/a	3.00	n/a
S5056-A17-93T	0.0043	NA	n/a	3.00	n/a
S5056-A18-94T <sup>(e)</sup>	0.0045	0.0019	n/a	2.92	n/a
<u>NO Samples:</u>			<u>≤ 0.0040</u>	<u>2.98</u>	<u>≤ 0.06</u>
S5056-A08-88T	0.0065	NA	n/a	3.00	n/a
S5056-A09-89T	0.0067	0.0061 x	n/a	3.00	n/a
S5056-A10-90T <sup>(e)</sup>	0.0072	0.0024	n/a	2.93	n/a
S5056-A16-92T	0.0065	NA	n/a	3.00	n/a
S5056-A17-93T	0.0049	0.0020	n/a	3.00	n/a
S5056-A18-94T <sup>(e)</sup>	0.0050	0.0024	n/a	2.92	n/a
<u>Gravimetric Samples:</u>			<u>50.3 mg</u>	<u>2.98</u>	<u>16.9 ± 0.2 mg/L</u>
S5056-A08-88T	n/a	n/a	50.4	3.00	16.8
S5056-A09-89T	n/a	n/a	49.9	3.00	16.6
S5056-A10-90T	n/a	n/a	49.9	2.93	17.0
S5056-A11-91T	n/a	n/a	50.5	3.00	16.8
S5056-A16-92T	n/a	n/a	50.3	3.00	16.8
S5056-A17-93T	n/a	n/a	50.7	3.00	16.9
S5056-A18-94T	n/a	n/a	50.0	2.92	17.1
S5056-A19-95T	n/a	n/a	51.0	3.00	17.0

- (a) Total blank-corrected analyte masses (nitrite for NO<sub>2</sub> 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  $\pm 1$  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 " $\leq$ " is defined in Section A.4.
- (d) NA = not analyzed; n/a = not applicable; x = not included in determination of average concentration.
- (e) NO<sub>x</sub> sorbent traps not preceded by an NH<sub>3</sub> 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.

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

## **Appendix B**

### **Tank Vapor Characterization:**

#### **Permanent Gases**

## Appendix B

### Tank Vapor Characterization: Permanent Gases

#### B.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02<sup>(a)</sup>. 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<sup>(b)</sup>, 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  $\mu\text{L}$  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<sup>(c)</sup> 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 ( $\text{H}_2$ ), carbon dioxide ( $\text{CO}_2$ ), carbon monoxide ( $\text{CO}$ ), methane ( $\text{CH}_4$ ), and nitrous oxide ( $\text{N}_2\text{O}$ ), 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  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$  using Helium ( $\text{He}$ ) as the carrier gas. A second GC analysis is performed for  $\text{H}_2$  (using nitrogen as the carrier gas) to enhance the signal sensitivity and lower the detection limit for this analyte. The permanent gases and the method detection limit (MDL) 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 <sub>2</sub>	PNL-TVP-05	25
Carbon Monoxide	CO	PNL-TVP-05	25
Methane	CH <sub>4</sub>	PNL-TVP-05	25
Hydrogen	H <sub>2</sub>	PNL-TVP-05	25
Nitrous Oxide	N <sub>2</sub> 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, CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub> over a range of 25 to 700 parts per million by volume (ppmv) using standards at five different concentrations and He as a carrier gas. A similar procedure was followed for H<sub>2</sub>, except the carrier gas was changed to N<sub>2</sub>. A least-squares linear-regression routine was applied to the calibration data set to generate the best-line fit for each compound.

Each analyte was quantitated by direct comparison of sample analyte peaks to the calibration plot generated for the compound. An MDL for the instrument has not been determined. The lowest calibration standard for each analyte is reported as the MDL. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within  $\pm 25\%$  of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N<sub>2</sub> reagent blank, an ambient air sample collected  $\sim 10$  m upwind of Tank T-110, 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 T-110, ambient air collected  $\sim 10$  m upwind of the tank, and ambient air collected through the VSS. The samples were analyzed September 7 through 11, 1995. Carbon dioxide, at 358 ppm, was the only permanent gas observed above the MDL in the tank headspace samples. Carbon dioxide in the headspace was at a similar concentration observed in the ambient air. A duplicate analysis was performed on SUMMA™ canister PNL 73; 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 T-110 and for Ambient Air and Ambient Air Through the VSS Collected Near Tank T-110 in SUMMA™ Canisters on 8/31/95

<u>Sample</u>	<u>Sample Matrix</u>	<u>PNL Canister Number</u>	<u>Sample Concentration (ppmv)</u>	<u>Average Concentration (ppmv)<sup>(a)</sup></u>
<u>CO<sub>x</sub> Samples:</u>				
S5056-A04-071	Tank	071	357	358
S5056-A12-073	Tank	073	356	
S5056-A20-088	Tank	088	361	
S5056-A12-073	Tank <sup>(b)</sup>	073	357	
S5056-A01-061	Ambient Air - Upwind	061	338	
S5056-A02-069	Ambient Air - VSS	069	331	
<u>CO Samples:</u>				
S5056-A04-071	Tank	071	<25	<25
S5056-A12-073	Tank	073	<25	
S5056-A20-088	Tank	088	<25	
S5056-A12-073	Tank <sup>(b)</sup>	073	<25	
S5056-A01-061	Ambient Air - Upwind	061	<25	
S5056-A02-069	Ambient Air - VSS	069	<25	
<u>CH<sub>4</sub> Samples:</u>				
S5056-A04-071	Tank	071	<25	<25
S5056-A12-073	Tank	073	<25	
S5056-A20-088	Tank	088	<25	
S5056-A12-073	Tank <sup>(b)</sup>	073	<25	
S5056-A01-061	Ambient Air - Upwind	061	<25	
S5056-A02-069	Ambient Air - VSS	069	<25	
<u>H<sub>2</sub> Samples:</u>				
S5056-A04-071	Tank	071	<25	<25
S5056-A12-073	Tank	073	<25	
S5056-A20-088	Tank	088	<25	
S5056-A12-073	Tank <sup>(b)</sup>	073	<25	
S5056-A01-061	Ambient Air - Upwind	061	<25	
S5056-A02-069	Ambient Air - VSS	069	<25	
<u>N<sub>2</sub>O Samples:</u>				
S5056-A04-071	Tank	071	<25	<25
S5056-A12-073	Tank	073	<25	
S5056-A20-088	Tank	088	<25	
S5056-A12-073	Tank <sup>(b)</sup>	073	<25	
S5056-A01-061	Ambient Air - Upwind	061	<25	
S5056-A02-069	Ambient Air - VSS	069	<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<sup>(a)</sup>. 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<sup>(b)</sup>, 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  $\mu$ L 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<sup>(c)</sup>, which is similar to U.S. Environmental Protection Agency (EPA) compendium Method TO-12. The method detection limits in the sub mg/m<sup>3</sup> are required to determine total nonmethanic organic compounds (TNMOC) concentration in the tank samples.

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

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- (a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Richland, Washington.
  - (b) Pacific Northwest Laboratory. 8/94. *Determination of TO-14 Volatile Organic Compounds in Ambient Air Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-01 (Rev. 0), PNL Technical Procedure, Richland, Washington.
  - (c) Pacific Northwest Laboratory. 6/95. *Determination of TO-12 Total Nonmethane Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Flame Ionization Detection*, PNL-TVP-08 (Rev. 0), PNL Technical Procedure, Richland, Washington.

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

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

### C.3 Quality Assurance/Quality Control

This method requires user calibration (category 2 measuring and test equipment) of the analytical system in accordance with PAP-70-1201, Calibration Control.

The TNMOC is calibrated by using propane as the calibration standard and using that response factor as an external standard method. The instrument calibration mixture for the PNL-TVP-08 analysis consists of National Institute for Standards and Technology (NIST) 99.999% propane analyzed using a 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/m<sup>3</sup> of TNMOCs. Second, an instrument continuing calibration run using 100-mL UHP propane analyzed using the response factor as an external standard method, followed by one blank volume of Aadco air.

**C.3.1 Quantitation Results of Target Analytes.** The mg/m<sup>3</sup> 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/m<sup>3</sup> concentrations are calculated from mg/m<sup>3</sup> 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.2 lists results of the TO-12 gas analysis from samples collected from the headspace of Tank T-110, ambient air collected ~ 10 m upwind of the tank, and ambient air collected through the vapor sampling system. The samples were analyzed on September 12, 1995. Concentrations in the ambient air samples ranged from 0.23 mg/m<sup>3</sup> to 0.26 mg/m<sup>3</sup>. Concentrations in the three tank headspace samples ranged from 0.96 mg/m<sup>3</sup> to 1.43 mg/m<sup>3</sup> with an average concentration of 1.12 mg/m<sup>3</sup>. This compares to 0.04 mg/m<sup>3</sup> 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 73; 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 T-110 and for Ambient Air and Ambient Air Through the VSS Collected near Tank T-110 in SUMMA™ Canisters on 8/31/95

Ambient Air Upwind		Ambient Air Through VSS		Tank Samples			Average Concentration Tank Samples
S5-056-A01.061 <sup>(a)</sup>	S5-056-A01.061 <sup>(a)</sup>	S5-056-A02.069 <sup>(a)</sup>	S5-056-A04.071 <sup>(a)</sup>	S5-056-A12.073 <sup>(a)</sup>	S5-056-A20.088 <sup>(a)</sup>	S5-056-A12.073 <sup>(a)</sup>	0.56
PNL 061 <sup>(b)</sup>	PNL 061 <sup>(b)</sup>	PNL 069 <sup>(b)</sup>	PNL 071 <sup>(b)</sup>	PNL 073 <sup>(b)</sup>	PNL 088 <sup>(b)</sup>	PNL 073 <sup>(b)(c)</sup>	
Concentration							
(mg/m <sup>3</sup> )							
0.13	0.12	0.12	0.72	0.48	0.49	0.49	

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 073; 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<sup>(a)</sup>. 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<sup>(b)</sup>, 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  $\mu$ 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<sup>(c)</sup>, 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- $\mu$ 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 organic analytes. 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 Procedure PNL-TVP-06<sup>(a)</sup>. The standard calibration mix was analyzed using four aliquot

**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

(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.

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 compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene- $d_5$ , and bromofluorobenzene was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank headspace samples are analyzed.

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

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

**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.

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

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

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

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

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

The IS level added to all blank, standard, and sample injections was 104 ppbv for bromochloromethane, 101 ppbv for 1,4-difluorobenzene, 98.5 ppbv for chlorobenzene-d<sub>5</sub>, and 104 ppbv for bromofluorobenzene. The IS concentrations were converted from ppbv to mg/m<sup>3</sup> at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, 117.6 for chlorobenzene-d<sub>5</sub>, 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 September 1, 1995, under Westinghouse Hanford Company (WHC) chain-of-custody 009254 (see Appendix F). The samples were analyzed on September 23, 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 T-110 and through the VSS near Tank T-110 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. Four target analytes above the 5-ppbv reporting cutoff and no TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. Only one of the four target analytes was identified in two or more tank headspace samples. Trichlorofluoromethane (0.04 mg/m<sup>3</sup>) accounted for 100% of the total concentration identified by both the target and TIC analyses. This compares to a total concentration of 1.12 mg/m<sup>3</sup> identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 73 was analyzed in replicate for target analytes and TICs to determine analytical precision. The relative percent difference (RPD) results are presented in Table D.3. The RPD was calculated for analytes detected above the detection limit and found in both replicates. One of two target analytes had an RPD of less than 10%.

Table D.4 lists the quantitative results for compounds listed as target analytes and TICs in ambient air and ambient air through the vapor sampling system. Traces of acetone and pyridine were identified in the ambient air sample. Acetone was also 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<sup>(a)</sup> and Tentatively Identified Compounds and Estimated Concentrations<sup>(b)</sup>, for Samples from the Headspace in Tank T-110 in SUMMA<sup>TM</sup> Canisters collected on 8/31/95

Target Analytes <sup>(b)</sup>	CAS No.	Mol Wt	Ret Time	S5056-A04.071 <sup>(c)</sup>		S5056-A12.073 <sup>(c)(d)</sup>		S5056-A20.088 <sup>(e)</sup>		Mean and Standard Deviations <sup>(b)</sup>	
				PNL 71 <sup>(e)</sup> (mg/m <sup>3</sup> ) (ppbv)	<0.01 <5	PNL 73 <sup>(e)(f)</sup> (mg/m <sup>3</sup> ) (ppbv)	<0.01 <5	PNL 88 <sup>(e)</sup> (mg/m <sup>3</sup> ) (ppbv)	0.01 6	(mg/m <sup>3</sup> ) (g)	St Dev (g)
Acetonitrile	75-05-8	41.1									
Trichlorofluoromethane	75-69-4	137.4		0.04	7	0.04	7	0.04	0.00	7	0.1
2-Butanone	78-93-3	72.1		<0.02	<5	0.03	8	<0.02	<5	<5	<5
Tridecane	629-50-5	184.4		0.06	7	<0.04	<5	<0.04	<5	<5	<5

**Tentatively**

**Identified Compound<sup>(b)</sup>**

No Compounds Found

- (a) TO-14 plus 22 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<sup>TM</sup> canister 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) 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.

**Table D.3. Positively Identified and Quantitated Target Analytes<sup>(a)</sup> and Tentatively Identified Compounds and Estimated Concentrations<sup>(b)</sup> of Replicate Analysis of a Single SUMMA<sup>TM</sup> Canister Collected from the Headspace of Tank T-110 on 8/31/95**

Target Analytes	CAS No.	Mol Wt	Ret Time	S5056-A12.073 <sup>(c)</sup>		S5056-A12.073 <sup>(c)</sup>		Relative Percent Difference <sup>(d)</sup> %
				PNL 73 <sup>(e)</sup> (mg/m <sup>3</sup> )	(ppbv)	PNL 73 <sup>(e)</sup> (mg/m <sup>3</sup> )	(ppbv)	
Acetonitrile	75-05-8	41.1		<0.01	<5	<0.01	<5	
Trichlorofluoromethane	75-69-4	137.4		0.04	7	0.05	8	22
2-Butanone	78-93-3	72.1		0.03	8	0.03	9	0
Tridecane	629-50-5	184.4		<0.04	<5	<0.04	<5	

**Tentatively Identified Compound<sup>(e)</sup>  
No Compounds Found**

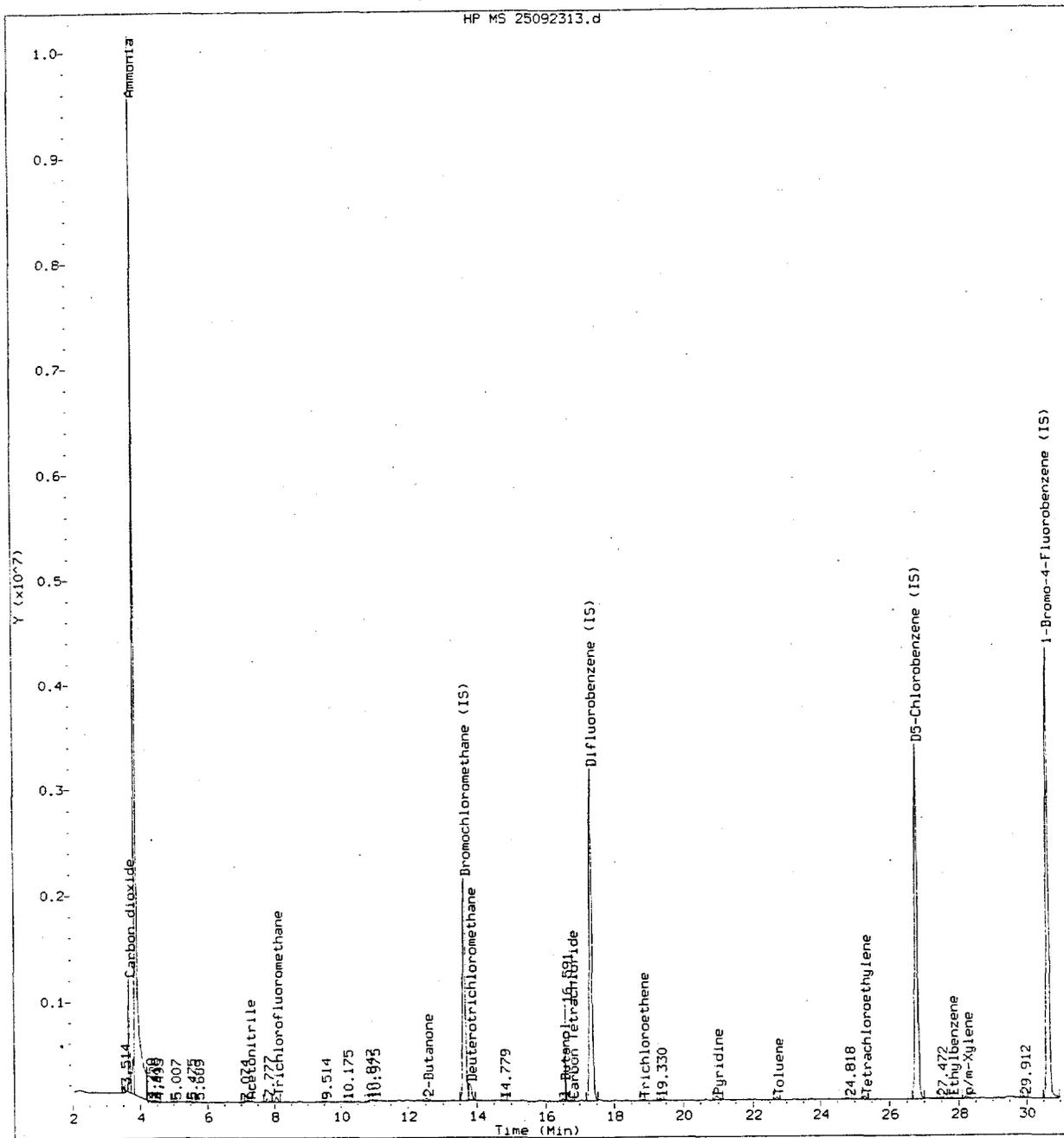
- (a) TO-14 plus 22 additional target analytes.
- (b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
- (c) WHC sample identification number.
- (d) PNL SUMMA<sup>TM</sup> canister number.
- (e) Obtained by mass spectral interpretation and comparison with the EPA/NIST and WILEY Libraries.
- (f) Relative percent differences (RPDs) based on mg/m<sup>3</sup> values; target analytic RPDs based on analytical values reported to two decimal places.

**Table D.4.** Positively Identified and Quantitated Target Analytes<sup>(a)</sup> and Tentatively Identified and Estimated Concentrations<sup>(b)</sup> in Ambient Air and Ambient Air Through the VSS Collected Near Tank T-110 in SUMMA™ Canisters on 8/31/95

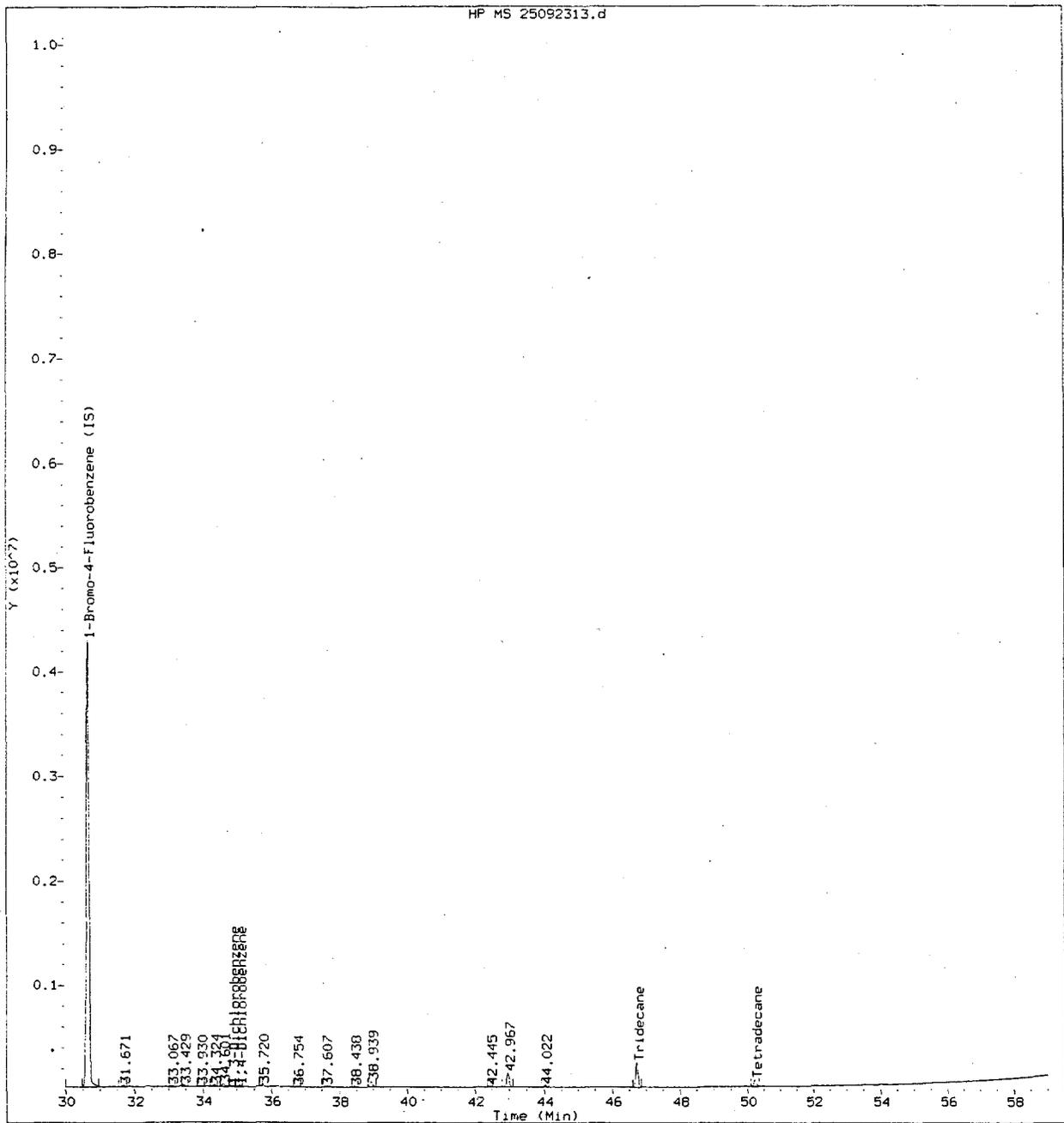
Target Analytes	CAS No.	Mol Wt	Ret Time	Ambient Air Upwind		Ambient Air Through VSS	
				PNL 61 <sup>(c)</sup> (mg/m <sup>3</sup> )	(ppbv)	PNL 69 <sup>(c)</sup> (mg/m <sup>3</sup> )	(ppbv)
Acetone	67-64-1	58.1		0.01	5	0.01	5
Pyridine	110-86-1	79.1		0.02	6	<0.02	<5

Tentatively Identified Compound<sup>(b)</sup>.  
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 T-110 SUMMA™ Canister Sample S5056-A04-071 Collected on 8/31/95



**Figure D.1b** Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank T-110  
SUMMA™ Canister Sample S5056-A04-071 Collected on 8/31/95

## **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 TD<sup>3</sup>), 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<sup>(a)</sup>, 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

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(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 61 compounds. These 61 compounds that are directly quantified in this analysis make up the target analyte list (these 61 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table E.1. The calibration mixture is prepared in common with the mixture used for the SUMMA™ analysis (see Section D.2). The standard calibration mix was analyzed using 4 aliquot sizes ranging from 100 mL to 1200 mL, and a response factor for each compound was calculated. Volumes of standard added to the traps are measured by pressure difference on a SUMMA™ canister of known volume. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. Performance-based detection limits for the target analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 parts per billion by volume (ppbv) is used.

**Table E.1** Target Organic Analytes

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

*NOTE: Compounds shown in italics have an exceptionally high volatility. They are routinely included in the standard and are quantified, but have a restricted linear dynamic range because of the potential for trap breakthrough.*

### E.3 Quality Assurance/Quality Control

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

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

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

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

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

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

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  $\text{mg/m}^3$  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  $\text{mg/m}^3$  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 bromofluorobenzene.

#### 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 September 1, 1995, under WHC chain-of-custody 009255. The samples were analyzed November 10 through 13, 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. Three target analytes above the 5-ppbv reporting cutoff and 2 TICs above the 10-ppbv reporting cutoff were detected in the tank headspace samples. One of 2 TICs was identified as an unknown. Trichlorofluoromethane ( $0.05 \text{ mg/m}^3$ ), methylene chloride ( $0.05 \text{ mg/m}^3$ ), and acetone ( $0.02 \text{ mg/m}^3$ ) accounted for 100% of the target analytes and 19% 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 ( $0.45 \text{ mg/m}^3$ ) and an unknown ( $0.05 \text{ mg/m}^3$ ), which accounted for 100% of the TICs and 81% of the total concentration identified by both the target and TIC analyses.

Triple sorbent trap sample PNL 663 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. All three target analytes had RPDs of less than 10%. Neither TIC had an RPD of less than 10%.

TST samples from Tank T-110 were analyzed using a protocol significantly different from that used on previous runs. The method used was generally consistent with the newly revised version of the method, TVP-10, Rev. 1. The method was in draft form at the time of analysis and was formally approved on November, 30, 1995. Because the traps were prepared and sent to the field prior to development of the new procedure, the surrogate preparation method was taken from the earlier revision (Rev. 0) which continued to produce erratic recoveries. Specific improvements include the following:

1. A 12-hour batch analysis is now used for all runs. A 12-hour clock starts with an autotune, CCV, BFB check, and continuing calibration blank (CCB). Following verification of the successful completion of QC checks, four samples were run. In this case the first batch contained two field and two trip blanks. The second batch used a new 12-hour clock with the same QC checks repeated. Three samples and one blank were then analyzed. QC checks for the two batches are treated independently

with respect to acceptance criteria. Both batches were included in a single computer batch file identified by the date for the start of work. Future runs will process and label 12-hour batches independently but use a single data package for reporting.

2. A revised group of quantitation ions was added to the method following a careful review of the EPA list of quantitation ions for related analytical methods combined with an empirical review of optimal quantitation ions for species not covered by EPA recommendations.
3. The chromatographic conditions were substantially modified through the use of subambient cooling of the GC oven with liquid nitrogen. This modification produced greatly improved chromatographic resolution and correspondingly better selectivity and sensitivity. The improved chromatographic resolution also greatly reduced the need for manual integration of peaks.
4. Initial calibrations are now based on a six-point calibration curve. The method requires that an ICV be run immediately following the initial calibration. For this run, the ICV used contained only TO-14 compounds and was of marginal quality. Two independently prepared ICV standards are on order and will be used in the future.

NOTE: The IS mixture as obtained from the commercial supplier (Scott) contains a fourth compound (bromochloromethane). Bromochloromethane is labeled on the chromatogram plots but not otherwise used in the method as it has exhibited erratic behavior when used as an IS. This situation is documented in the current revision of TVP-10.

Following completion of analysis, it was noted that retention times of the first internal standards and surrogates were shifted for the second field blank and both trip blanks. The cause of the shift is believed to be caused by a time out of the cryo-cooling of the GC, which was not detected at the time by the analyst because of limited experience with the cryogenic operation. That potential problem has been corrected for future runs through amendments to the method and the use of a checklist including a temperature check before beginning each individual run. The effect on the data was minimal since a manual correction could be performed, and the samples were blanks with no detectable target analytes present. The IS checks were satisfactory according to currently accepted criteria ( $\pm 50\%$  relative to initial CCV) for all samples in both batches except the first CCB, which had a higher than expected IS response. The CCB showed very minor traces of carryover from the CCV but was otherwise within tolerance. The field and trip blanks were clean of target compounds except for a trace of methylene chloride and toluene in the first field blank. Both field blanks and first trip blank 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 moderately high levels and has been a persistent apparent artifact in previous samples taken over the last few months. It probably represents an erratic storage artifact most likely associated with fugitive emissions of refrigerant. The CCV checks were generally satisfactory for most compounds in both CCVs. Specific exceptions included: CCV-1 (bromomethane, acetone, and pyridine) and CCV-2 (bromomethane, pyridine, trans-1,3-dichloropropene, and tetradecane). Lab blanks were clean. The surrogate recoveries were erratic as a result of a continuing problem with surrogate preparation which resulted in a substantial modification of the surrogate preparation technique to be used on all future jobs.

Organic loading was negligible for these samples with only traces of a number of target compounds reported. The first sample continued to show detectable tributyl phosphate (TBP) but at much lower levels than formerly observed. The TBP peaks were completely absent from the other two samples and repeat. This pattern has been present in all tanks sampled with TSTs after AX-103. It appears likely that this is a sampling artifact which has been gradually diminishing over time with continued use of the VSS sample manifold.

Table E.2. Positively Identified and Quantitated Target Analytes<sup>(a)</sup> and Tentatively Identified Compounds and Estimated Concentrations<sup>(b)</sup> for Triple Sorbent Traps Collected from the Headspace of Tank T-110 on 8/31/95.

Target Analytes <sup>(a)</sup>	CAS No.	Mol Wt	Ret Time	S5056-A05.662 <sup>(c)</sup>		S5056-A06.663 <sup>(c)(d)</sup>		S5056-A07.664 <sup>(c)</sup>		Mean and Standard Deviations <sup>(e)</sup>			
				PNL 662 <sup>(e)</sup> (mg/m <sup>3</sup> )	(ppbv)	PNL 663 <sup>(e)</sup> (mg/m <sup>3</sup> )	(ppbv)	PNL 664 <sup>(e)</sup> (mg/m <sup>3</sup> )	(ppbv)	(mg/m <sup>3</sup> )	St Dev (ppbv)	St Dev	St Dev
Acetone	67-64-1	58.1	9.1	0.02	8	0.02	7	0.02	6	0.02	0.00	7	0.7
Trichlorofluoromethane	75-69-4	137.4	14.8	0.05	8	0.05	8	0.05	8	0.05	0.00	8	0.3
Methylene Chloride	75-09-2	84.9		0.08	22	0.03	7	0.04	11	0.05	0.03	13	7.6
<b>Tentatively Identified Compound<sup>(b)</sup></b>													
Ethane, 1-chloro-1,1-difluoro-Unknown	75-68-3	100	9.1	0.923	207	0.261	58	0.166	37	0.45	0.41	101	92.4
			14.8	0.100	(h)	0.027	(h)	0.016	(h)	0.05	0.05	(g)	(g)

- (a) TO-14 plus 22 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.

**Table E.3. Positively Identified and Quantitated Target Analytes<sup>(a)</sup> and Tentatively Identified Compounds and Estimated Concentrations<sup>(b)</sup>  
Results of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank T-110 on 8/31/95**

Target Analytes <sup>(b)</sup>	CAS No.	ol. Wt	Ret Time	S5056-A06.663 <sup>(c)</sup>		S5056-A06.663 <sup>(c)</sup>		Relative Percent Difference <sup>(g)</sup> %
				(mg/m <sup>3</sup> )	(ppbv)	(mg/m <sup>3</sup> )	(ppbv)	
Acetone	67-64-1	58.1		0.02	7	0.02	7	0
Trichlorofluoromethane	75-69-4	137.4		0.05	8	0.05	8	0
Methylene Chloride	75-09-2	84.9		0.03	7	0.03	8	0
<b>Tentatively Identified Compound<sup>(c)</sup></b>								
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	9.1	0.261	58	0.230	52	13
Unknown			14.8	0.027	(f)	0.031	(f)	14

- (a) TO-14 plus 22 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/m<sup>3</sup> 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.
- (h) Target analyte ppb values reported to two decimal places, but rounded to the whole integer in individual TST sample results.

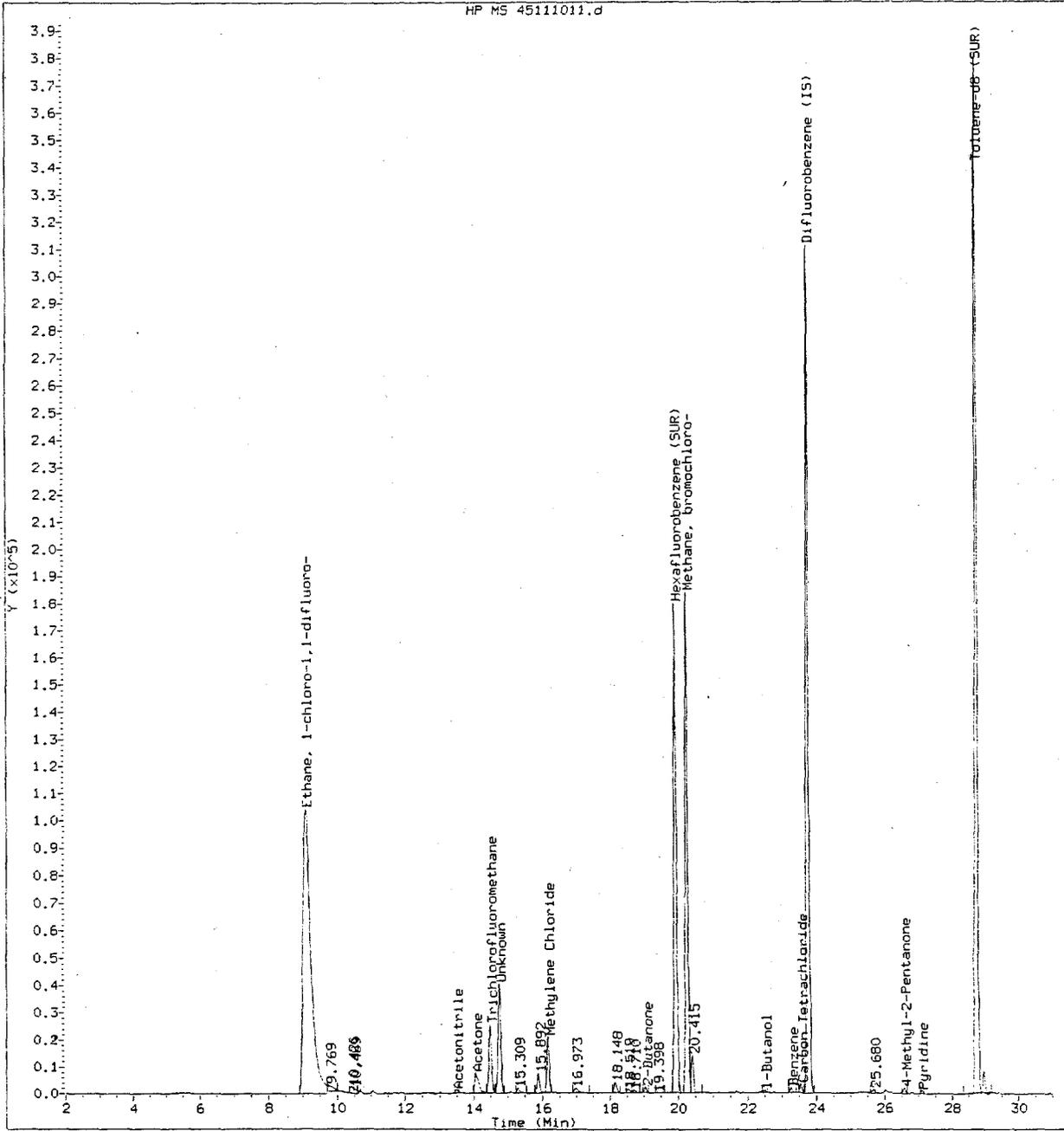
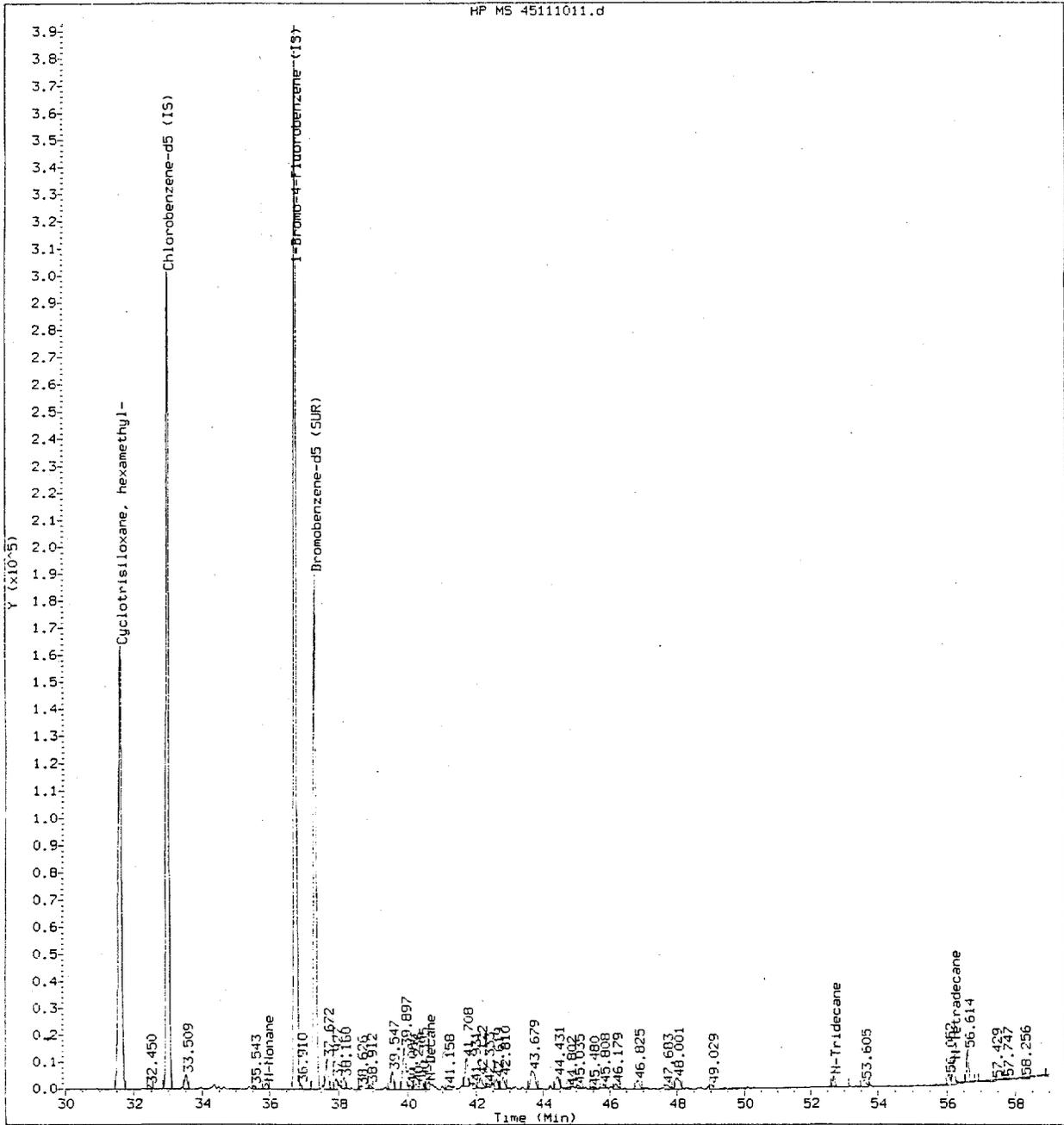


Figure E.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank T-110 Triple Sorbent Trap Sample S5056-A06-663 Collected on 8/31/95



**Figure E.1b** Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank T-110 Triple Sorbent Trap Sample S5056-A06-663 Collected on 8/31/95

## **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 Collection date 08 - 31 - 95  
241-T-110 Tank Vapor Sample SAF S5056 Preparation date 08 - 09 - 95  
(VSS Truck)

Ice Chest No. Field Logbook No. WHC-J-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

S5056 - A08 . 88T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O	(INORG Sorbent Trap # 1)
S5056 - A09 . 89T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O	(INORG Sorbent Trap # 2)
S5056 - A10 . 90T	NO <sub>x</sub> /H <sub>2</sub> O	(INORG Sorbent Trap # 3)
S5056 - A11 . 91T	NH <sub>3</sub> /H <sub>2</sub> O/H <sub>2</sub> O	(INORG Sorbent Trap # 4)
S5056 - A16 . 92T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O	(INORG Sorbent Trap # 5)
S5056 - A17 . 93T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O	(INORG Sorbent Trap # 6)
S5056 - A18 . 94T	NO <sub>x</sub> /H <sub>2</sub> O	(INORG Sorbent Trap # 7)
S5056 - A19 . 95T	NH <sub>3</sub> /H <sub>2</sub> O/H <sub>2</sub> O	(INORG Sorbent Trap # 8)
S5056 - A25 . 96T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O	(INORG Field Blank # 1)
S5056 - A26 . 97T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> O	(INORG Field Blank # 2)
S5056 - A27 . 98T	NH <sub>3</sub> /NO <sub>x</sub> /H <sub>2</sub> 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>J.W.D.</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.R. Utell <i>T.R. Utell</i>	08-09-95	1445
<del>T.R. Utell</del>	<del>08-31-95</del>	<del>0900</del>	<del>H.C.D. / G.S. Carr</del>	<del>08-31-95</del>	<del>0900</del>
<del>H.C.D. / G.S. Carr</del>	<del>09-01-95</del>	<del>1050</del>	<del>J A Edwards / T.R. Utell</del>	<del>9-1-95</del>	<del>1050</del>
J A Edwards <i>J A Edwards</i>	9-6-95	1545	G.W. Dennis <i>J.W.D.</i>	9-6-95	1545
G.W. Dennis <i>J.W.D.</i>	9-7-95	1345	K.H. Pool <i>Karl Pool</i>		1345

Final Sample Disposition

Comments:

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

Custody Form Initiator J. A. Edwards - PNL  
 Company Contact R. D. Mahon - WHC  
 Project Designation/Sampling Locations 200 West Tank Farm  
 241-T-110 Tank Vapor Sample SAF S5056  
 (VSS Truck)  
 Ice Chest No.  
 Bill of Lading/Airbill No. N/A  
 Method of Shipment Government Truck  
 Shipped to PNL  
 Possible Sample Hazards/Remarks Unknown at time of sampling

Telephone (509) 373-0141  
 Page 85-3009 / FAX 376-0418  
 Telephone (509) 373-2891  
 Page 85-3152 / FAX 373-3793  
 Collection date 08 - 31 - 95  
 Preparation date 08 - 11 - 95  
 Field Logbook No. WHC-N-647-10  
 Offsite Property No. N/A

Sample Identification

S5056 - A01 . 061 Ambient Air SUMMA #1 Upwind of T-110  
 S5056 - A02 . 069 Ambient Air SUMMA #2 Through Port # 15  
 S5056 - A04 . 071 SUMMA #3 Port # 15  
 S5056 - A12 . 073 SUMMA #4 Port # 15  
 S5056 - A20 . 088 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	08-14-95	0925	T.B. Utecht	08-14-95	0925	
T.B. Utecht	08-31-95	0900	J.D. Caprio	08-31-95	0900	
J.D. Caprio	09-31-95	1045	J.A. Edwards	9-1-95	1045	

Final Sample Disposition

Comments:

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

(Revised 10/17/94 PNL)

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

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

Project Designation/Sampling Locations 200 West Tank Farm Collection date 08 - 31 - 95  
241-T-110 Tank Vapor Sample SAF S5056 Preparation date 08 - 01 - 95  
(VSS Truck)

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

Erico Hi/Lo thermometer No. PNL-T-004

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

S5056 - A05 . 662 . PNL Triple Sorbent Trap (TST) Sample # 1  
S5056 - A06 . 663 . PNL TST Sample # 2  
S5056 - A07 . 664 . PNL TST Sample # 3

S5056 - A13 . 665 . PNL TST Sample # 4  
S5056 - A14 . 666 . PNL TST Sample # 5  
S5056 - A15 . 667 . PNL TST Sample # 6

S5056 - A21 . 668 . Open, close & store PNL TST Field Blank # 1 In VSS truck  
S5056 - A22 . 669 . Open, close & store PNL TST Field Blank # 2 In VSS truck

S5056 - A23 . 670 . Store PNL TST Trip Blank # 1 None  
S5056 - A24 . 671 . Store PNL TST Trip Blank # 2 None

[ ] Field Transfer of Custody		[ ] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
J.A. Edwards / J.A. Edwards	08-09-95	1420	T.B. Utter / T.B. Utter	08-09-95	1420
T.B. Utter / T.B. Utter	08-21-95	0900	A.J. Cline / G.S. Cline	08-31-95	0900
G.S. Cline / G.S. Cline	09-01-95	1055	J.A. Edwards / J.A. Edwards	9-1-95	1055

Final Sample Disposition

Comments:

- PNL (only) Checklist
- 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? (<5°C)  Y / N
  - Hi/Lo thermometer - *Keep upright!*  Y / N
  - Hi/Lo thermometer /  Y / N
  - Rad release stickers on samples? /  Y / N
  - Activity report from 222S? /  Y / N
  - COC copy for LRB, RIDS filed? /  Y / N

Comments:

Cooler Temperature Status

Hi -15 °C / Lo -15 °C (pick up at PNL to WHC) |

Hi \_\_\_ °C / Lo \_\_\_ °C (delivery at WHC from PNL) |

Hi \_\_\_ °C / Lo \_\_\_ °C (at return to PNL from WHC) |

Hi +17 °C / Lo +2 °C (at delivery from WHC to PNL) |

POC  POC

(Revised 06/21/95 PNL)

## Distribution List

PNNL-10958

### PNNL

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

### Lockheed

Larry Pennington	S7-21
Luther Buckley	R2-12

### DOE-RL

Carol Babel	S7-54
Jim Thompson	S7-54