

# 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-BX-110: Results from Samples Collected on 04/30/96

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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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## **TANK VAPOR CHARACTERIZATION PROJECT**

### **Headspace Vapor Characterization of Hanford Waste Tank 241-BX-110: Results from Samples Collected on 4/30/96**

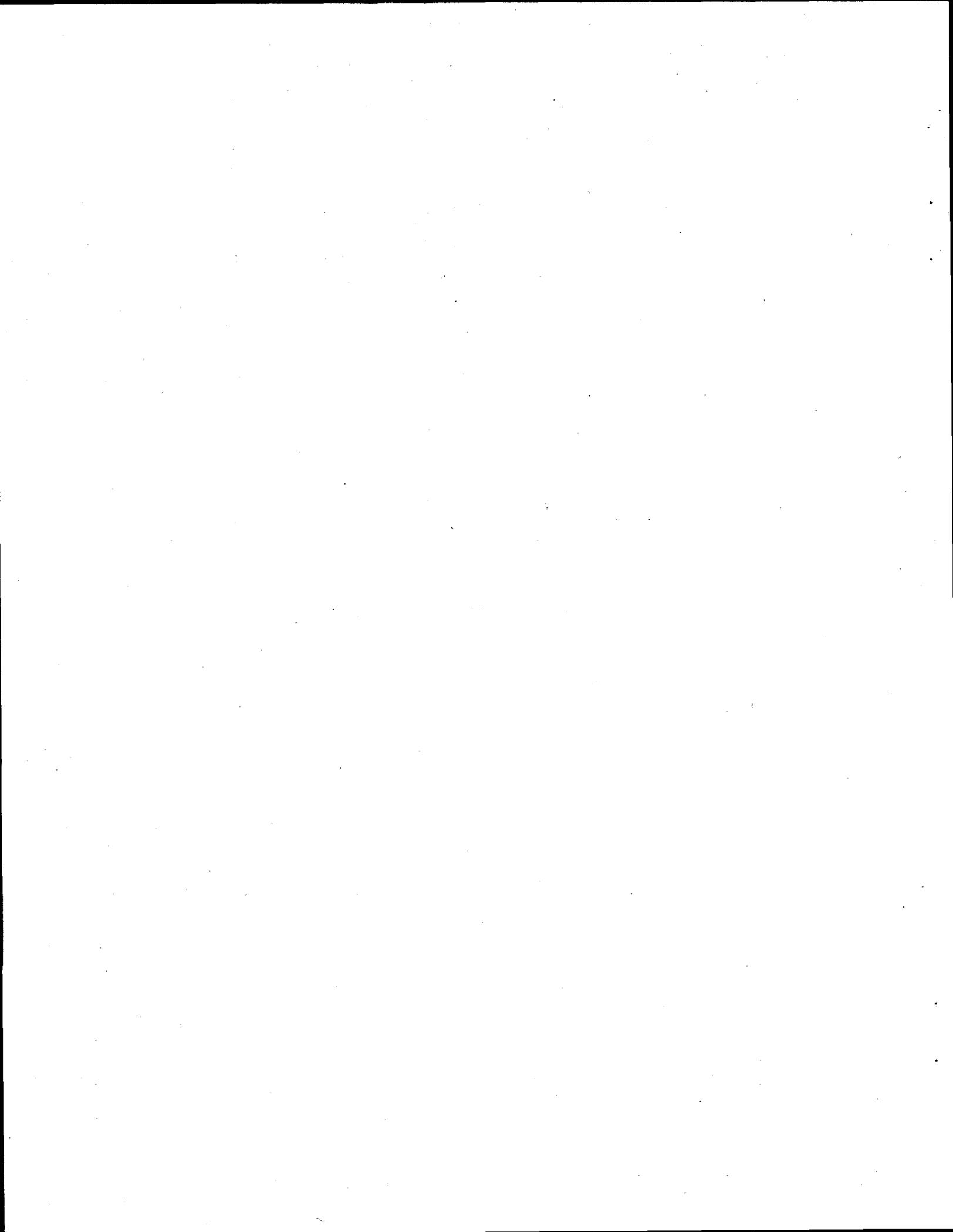
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## Summary

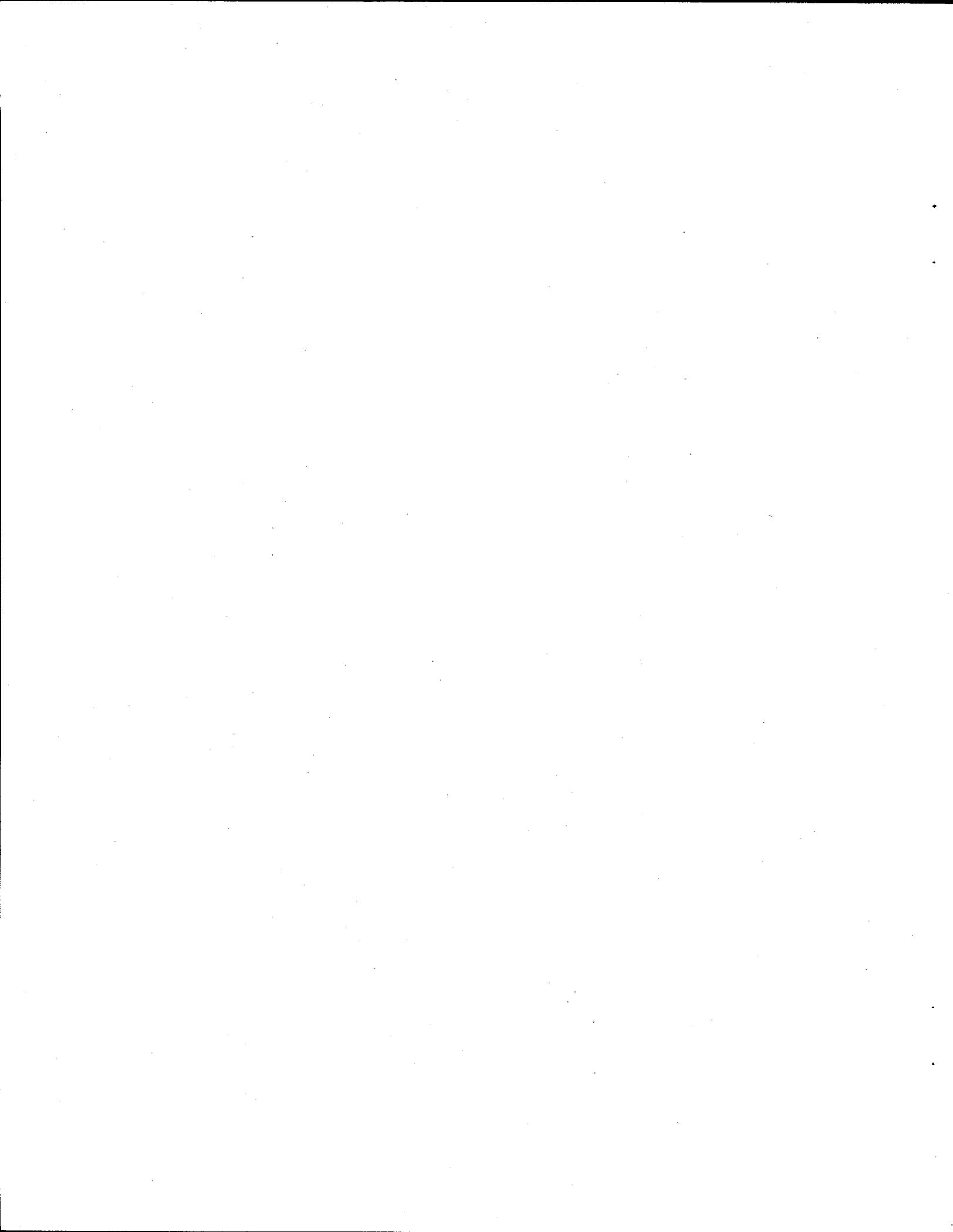
This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-BX-110 (Tank BX-110) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support 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, sample volumes provided by WHC. A summary of the inorganic analytes, permanent gases, and total non-methane organic compounds is listed in Table S.1. The three highest concentration analytes detected in SUMMA™ canister and triple sorbent trap samples are also listed in Table S.1. Detailed descriptions of the analytical results appear in the appendices.

**Table S.1.** Summary Results of Samples to Characterize the Headspace of Tank BX-110 on 4/30/96

<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>	63 ± 3	ppmv
		NO <sub>2</sub>	< 0.15	ppmv
		NO	< 0.15	ppmv
		H <sub>2</sub> O	8.9 ± 0.3	mg/L
Permanent Gases	SUMMA™ Canister	CO <sub>2</sub>	< 17	ppmv
		CO	< 17	ppmv
		CH <sub>4</sub>	< 25	ppmv
		H <sub>2</sub>	< 17	ppmv
		N <sub>2</sub> O	< 17	ppmv
Total Non-Methane Organic Compounds (TO-12)	SUMMA™ Canister	Non-Methane Organic Compounds	1.96	mg/m <sup>3</sup>
Volatile Organics (TO-14)	SUMMA™ Canister		0.957	ppmv
		Methanol	0.745	ppmv
		Ethanol	0.188	ppmv
Semi-Volatile Organics (PNL-TVP-10)	Sorbent Traps		0.294	ppmv
		Methanol	0.270	ppmv
		Ethanol	0.130	ppmv
		Acetone		

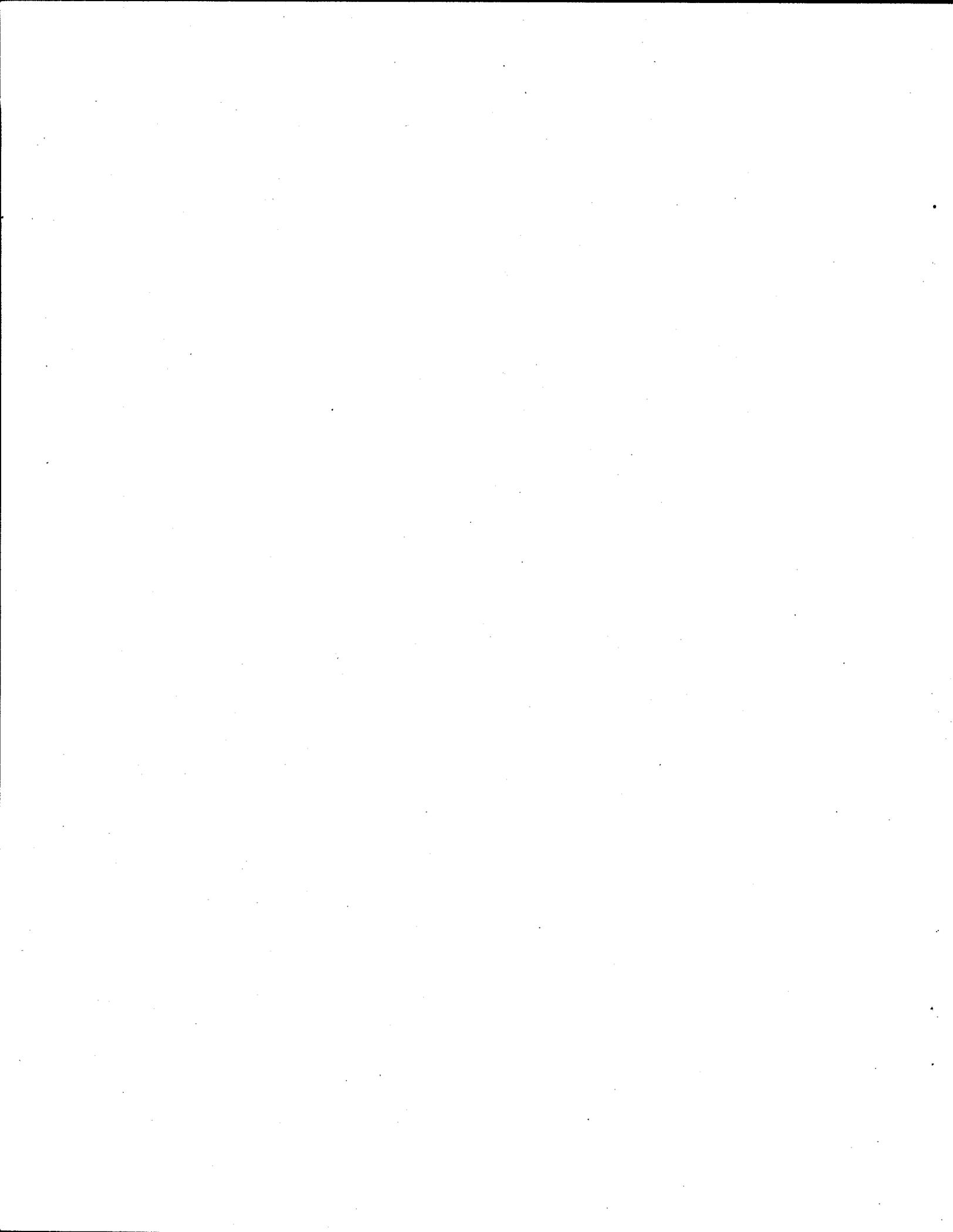
(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data.

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



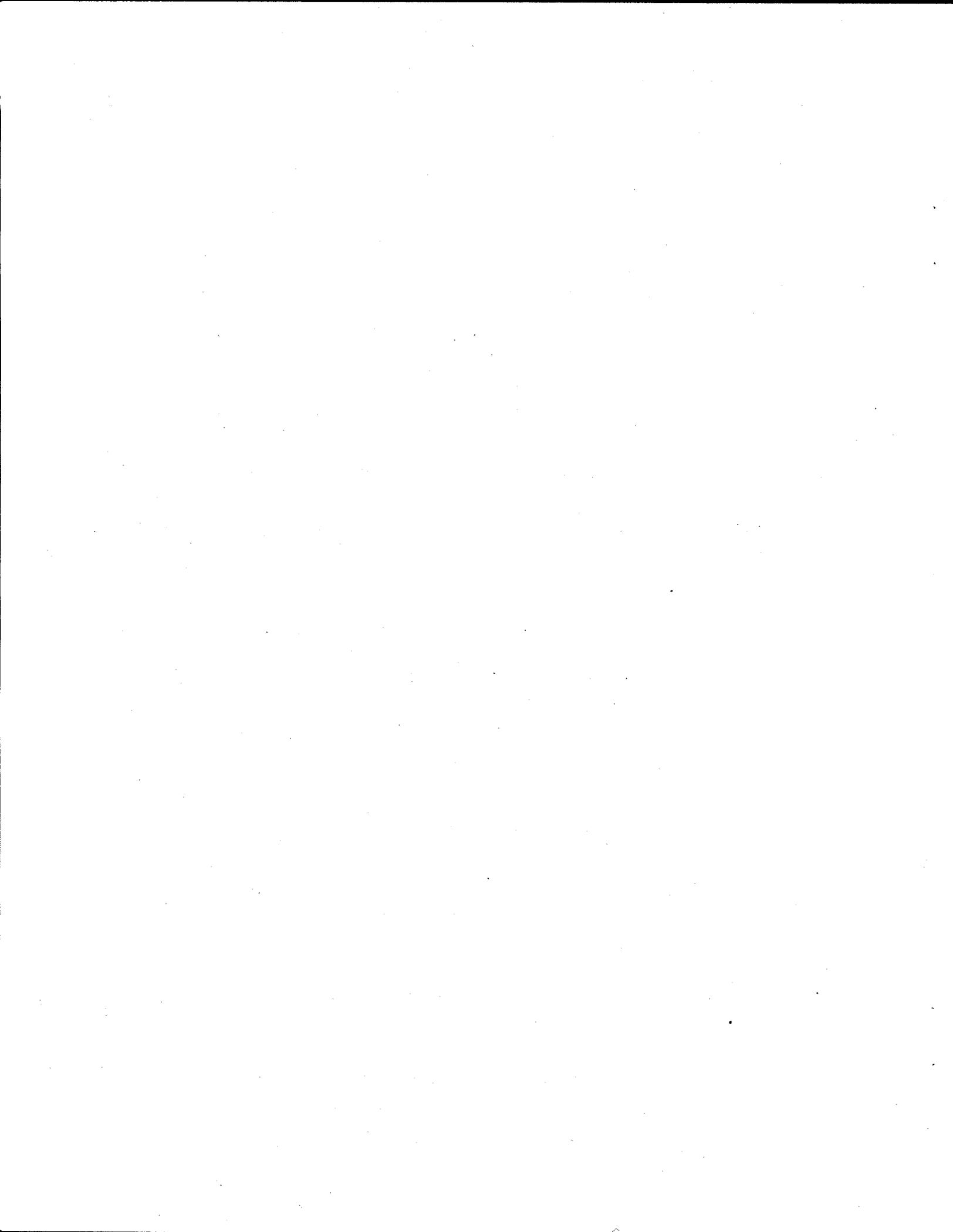
## Acknowledgments

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

% D	% Difference
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 non-methane organic compounds
TST	triple sorbent trap
UHP	ultra high purity
VAL	Vapor Analytical Laboratory
VSS	vapor sampling system
WHC	Westinghouse Hanford Company



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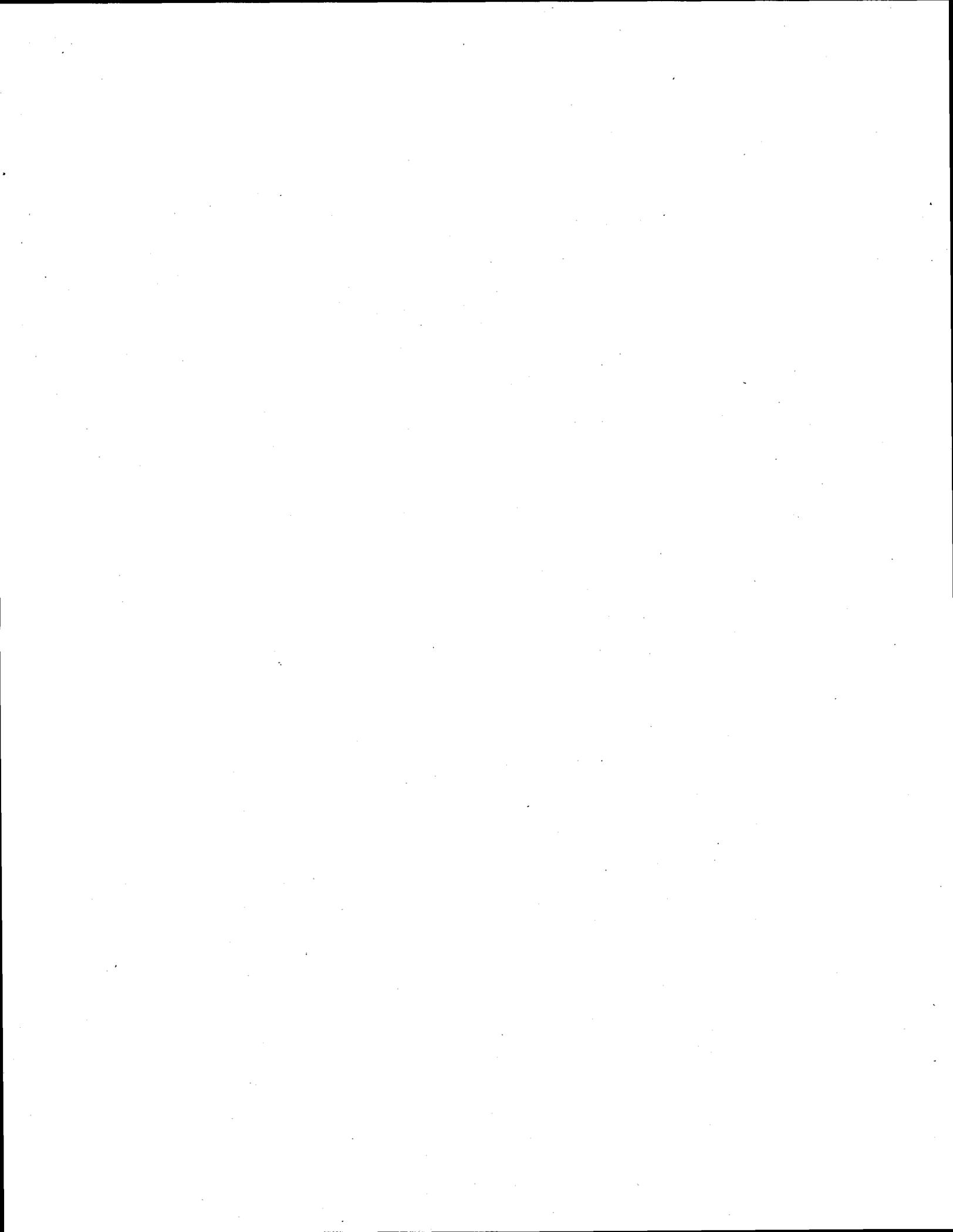
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## 1.0 Introduction

This report describes the results of vapor samples taken from the headspace of waste storage tank 241-BX-110 (Tank BX-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 S6046. Samples were collected by WHC on April 30, 1996 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 six sorbent trains for selected inorganic analytes (four sample trains and two field blanks), five SUMMA™ canisters for permanent gases and volatile organic analytes (three samples and two ambient canisters), and eight triple sorbent traps (TSTs) for semi-volatile organic analytes (four samples, two field blanks, and two trip blanks). The samples and controls were provided to WHC on April 29, 1996. Exposed samples and controls were returned to PNNL on May 15, 1996. 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 organic compounds* using cryogenic preconcentration followed by gas chromatography/flame ionization detection (GC/FID)
- *volatile organic analytes* analyses using cryogenic preconcentration followed by gas chromatograph/mass spectrometer (GC/MS)

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

(b) PNL-TVP-07, Rev. 2, December 1995, *Sample Shipping and Receiving Procedure for PNL Waste Tank Samples*, PNL Technical Procedure, Tank Vapor Project, Pacific Northwest Laboratory, Richland, Washington.

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

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

## 2.0 Analytical Results

Samples obtained by WHC from the headspace of Tank BX-110 on April 30, 1996 (Sample Job S6046) 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 appendices.

### 2.1 Inorganic Analytes

The vapor concentrations of selected inorganic analytes ( $\text{NH}_3$ ,  $\text{NO}_2$ , and  $\text{NO}$ ) 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  $63 \pm 3$  ppmv ( $\text{NH}_3$ ),  $< 0.15$  ppmv ( $\text{NO}_2$ ),  $< 0.15$  ppmv ( $\text{NO}$ ), and  $8.9 \pm 0.3$  mg/L (primarily  $\text{H}_2\text{O}$ ). The vapor concentration results were based on four samples for each compound. All samples (100%) were successfully analyzed and used in the averages. Representative field blanks were also analyzed and used to correct data.

Results provided above are estimated to be accurate to within  $\pm 10\%$  (assuming negligible error in the sample volume measurements) and are within the  $\pm 30\%$  specified by the SAP. Measurement precision, as indicated by the relative standard deviation, was 5% for the compounds found to be present at concentrations greater than the analytical method estimated quantitation limit (EQL), and within the 25% specified by the SAP. These uncertainties were confirmed by evaluation of spikes and continuing calibration standards ( $\text{NH}_3$  and  $\text{NO}_2$ ) and evaluation of the variability of field blanks ( $\text{H}_2\text{O}$ ). All samples were analyzed within 23 days after being collected. No deviations from standard procedures were noted. Data and additional information on samples, analyses, and results are described in Appendix A. The COC form used to control samples, 100080, is included in Appendix F.

### 2.2 Permanent Gases

The complete results of the permanent gas analysis of Tank BX-110 can be found in Appendix B. In summary, no permanent gases were observed in the tank headspace samples.

### 2.3 Total Non-Methane Organic Compounds

The complete results of the TO-12 analysis of Tank BX-110 can be found in Appendix C. In summary, the average concentration in the three tank headspace samples was  $1.96 \text{ mg/m}^3$ . This compares to  $3.76 \text{ mg/m}^3$  for the sum of all target compounds and tentatively identified compounds (TICs) identified in the analysis of the SUMMA™ canisters.

## 2.4 Organic Analytes by SUMMA™ Method

The complete results of the SUMMA™ analysis of Tank BX-110 can be found in Appendix D. In summary, twenty-two target analytes above the instrument detection limit (IDL) and two TICs were detected in the tank headspace samples. Seventeen target analytes and one TIC were identified in two or more tank headspace samples. Ethanol at 1.53 mg/m<sup>3</sup> and methanol at 1.37 mg/m<sup>3</sup> accounted for 77% of the compounds identified in the analysis. The total concentration of the target analytes was found to be 3.75 mg/m<sup>3</sup>. The total concentration of all the compounds identified was 3.76 mg/m<sup>3</sup>. This compares to a total concentration of 1.96 mg/m<sup>3</sup> identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 213 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 IDL and found in both replicates. Six of 15 compounds had RPDs of less than 10%.

Twelve compounds were observed in one or both of the ambient air samples. The trace levels of many of the target compounds was believed to be caused by carry-over from the calibration standard.

## 2.5 Organic Analytes by Triple Sorbent Trap Method

The complete results of the sorbent trap analysis of Tank BX-110 can be found in Appendix E. In summary, 17 target analytes above the IDL and three TICs were detected in the tank headspace samples. Sixteen of the target analytes and all TICs were observed in two sorbent traps. Methanol at 0.42 mg/m<sup>3</sup> and ethanol at 0.56 mg/m<sup>3</sup> accounted for 57% of the target analytes and 50% of the total concentration identified by the analyses. The total concentration of the target analytes was found to be 1.72 mg/m<sup>3</sup> or 88% of the total concentration identified by the analyses. The total concentration of all the compounds identified was 1.97 mg/m<sup>3</sup>.

Triple sorbent trap sample PNL 970 was analyzed in replicate for target analytes and TICs to determine analytical precision. The RPD results are presented in Table E.3. The RPD was calculated for analytes detected above the detection limit and found in both replicates. Nine of 16 target analytes had RPDs of less than 10%.

### 3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank BX-110 collected on April 30, 1996 (Sample Job S6046). 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 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. 2, Westinghouse Hanford Company, Richland, Washington.

### Further Reading

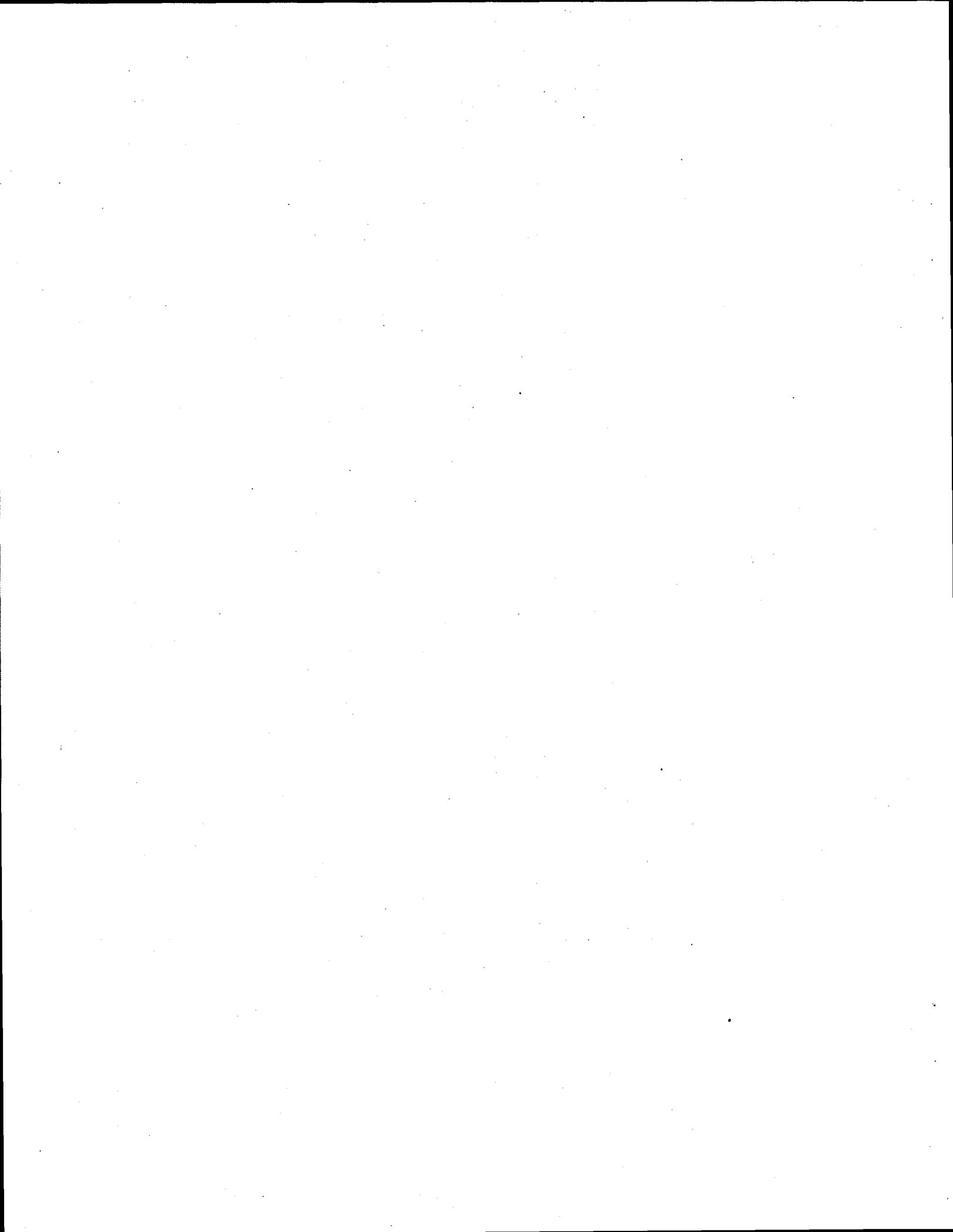
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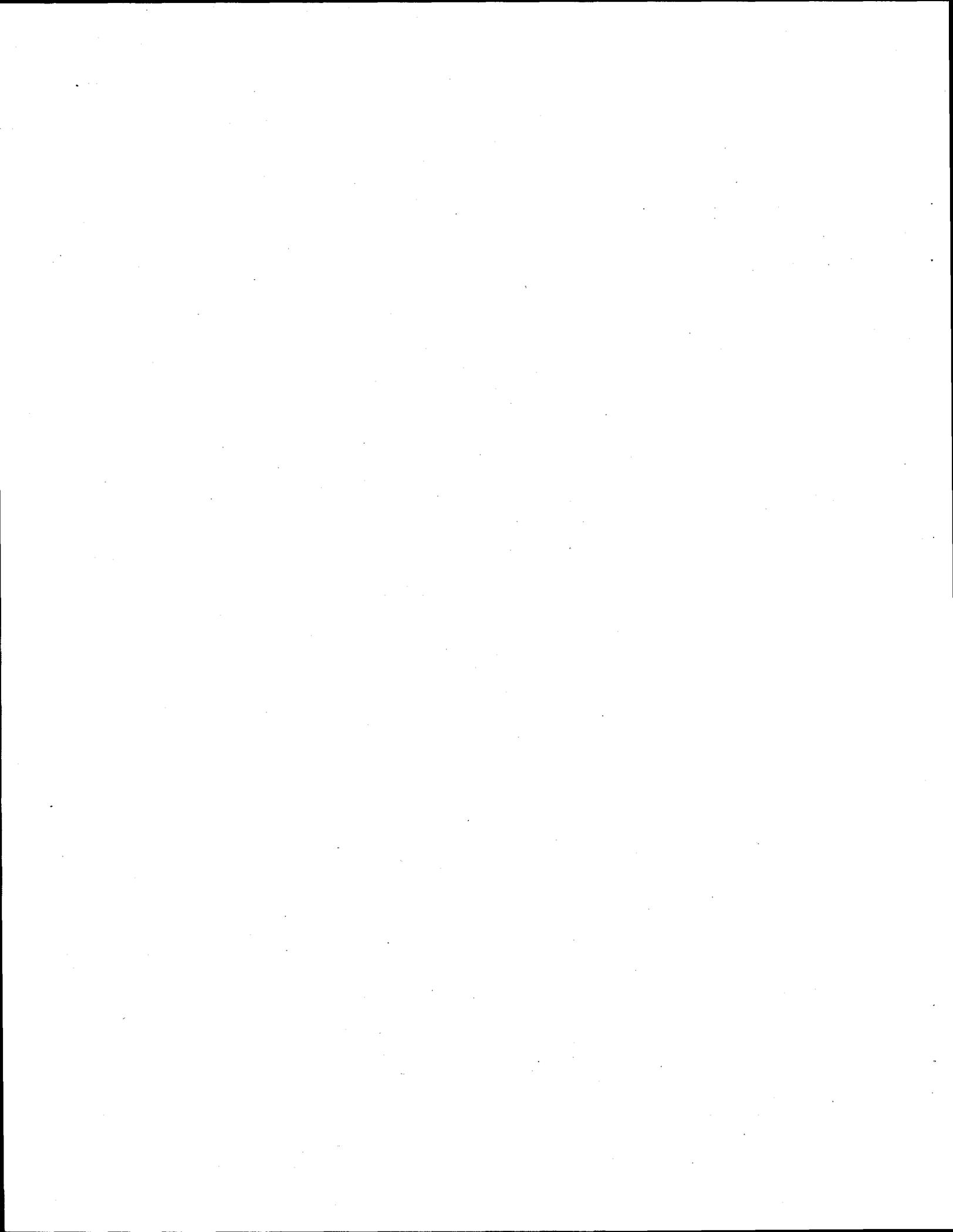
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## **Appendix A**

### **Tank Vapor Characterization:**

### **Inorganic Analytes**



## Appendix A

### Tank Vapor Characterization: Inorganic Analytes

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to Westinghouse Hanford Company (WHC) for sampling the tank headspace using the Vapor Sampling System (VSS). Blanks, spiked blanks (when requested), and exposed samples were returned to Pacific Northwest National Laboratory (PNNL) for analysis. Analyses were performed to provide information on the tank headspace concentration of the following analytes: ammonia ( $\text{NH}_3$ ), 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 sorbent tubes 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 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, with 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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<sup>(a)</sup> Pacific Northwest Laboratory. 12/95. *Sorbent Trap Preparation for Sampling and Analysis: Waste Tank Inorganic Vapor Samples*, PNL-TVP-09 (Rev. 2), PNL Technical Procedure, Pacific Northwest Laboratory, 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 that has 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 moles. 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.

**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 Rev. 0<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). Electromotive force (volts) 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 one separator column, and 3) all standards, samples, and blanks were 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 in accordance with procedure PNL-TVP-09. 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. Field blanks were used to correct results.

### A.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNNL documents including PNL-MA-70 (Part 3), PNL-ALO-212, PNL-ALO-226, and Quality Assurance Plan ETD-002. The samples were analyzed following PNNL Impact Level II. 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 EQL 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 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, Quantification Limits, and Notification Levels for Selected Inorganic Analytes<sup>(a)</sup>**

Analyte	Formula	Procedure	EQL <sup>(b)</sup> ( $\mu\text{g}$ )	EQL <sup>(b)</sup> (ppmv)	Notification Level <sup>(c)</sup> (ppmv)
Ammonia	NH <sub>3</sub>	PNL-ALO-226	1.0	0.66	$\geq 150$
Nitrogen Dioxide	NO <sub>2</sub>	PNL-ALO-212	0.3	0.15	$\geq 10$
Nitric oxide	NO	PNL-ALO-212	0.3	0.15	$\geq 50$
Mass (water) <sup>(d)</sup>	n/a	PNL-TVP-09	0.6 mg	0.3 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) The lowest calibration standard is defined as the EQL.
- (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 BX-110 on April 30, 1996 using the VSS. The sample job designation number was S6046. 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 COC form 100080 (Appendix D). The inorganic samples and sample volume information were received from WHC on May 15, 1996. Analyses were completed on May 20, 1996 (gravimetric, 20 days elapsed), May 22, 1996 (ammonia, 22 days elapsed), and May 23, 1996 (nitrite, 23 days elapsed).

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, corrected for blanks, were less than the EQL in Table A.1, the concentration results (Table A.3) are listed as "less-than" the EQL value. 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  $63 \pm 3$  ppmv, based on all four samples. The blank-corrected  $\text{NH}_3$  quantities in the sorbent traps ranged from 5.21 to 5.86  $\mu\text{mol}$  in front sections; blank-corrected  $\text{NH}_3$  was not found ( $\leq 0.01 \mu\text{mol}$ ) in back sorbent sections. Blank corrections, 0.095  $\mu\text{mol}$  in front and 0.06  $\mu\text{mol}$  in back sections, were about 0.5% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of  $\pm 0.4\%$ . One blank sorbent trap was spiked with 17  $\mu\text{g}/\text{mL}$  of  $\text{NH}_3$  and yielded a percentage recovery of 103%. One sample leachate was spiked after initial analysis with roughly the quantity of ammonia in the sample and yielded a percentage recovery of 92%. The initial and continuing calibration verification standards, using NIST-traceable material, yielded percentage recoveries of 100% (ICV) and 103 and 102% (CCV) during the analytical session. A 5-point calibration was performed over an  $\text{NH}_3$  range of 0.1 to 1000  $\mu\text{g}/\text{mL}$ .

**A.4.2 Nitrogen Oxides Results.** The concentrations of  $\text{NO}_2$  and  $\text{NO}$  were both  $< 0.15$  ppmv based on all four samples. Blank-corrected  $\text{NO}_2^-$  quantities in the sorbent traps averaged  $< 0.013 \mu\text{mol}$ . Nitrite blank levels used to correct data were 0.0109  $\mu\text{mol}$  in front (four of four blanks analyzed) and 0.0055  $\mu\text{mol}$  in back (two of four blanks analyzed) sorbent sections. The analyses of two samples were duplicated and yielded repeatabilities of  $\pm 0\%$  and  $\pm 1.0\%$ . Two sample leachates were spiked with 0.25 ppm  $\text{NO}_2^-$  and yielded percentage recoveries of 106 and 106%. A 4-point calibration was performed over a concentration range of 0 to 0.5  $\mu\text{g NO}_2^-$  per mL in the desorbing matrix. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74  $\mu\text{mol NO}_2^-$  during previous sample jobs yielded percentage recoveries of  $153 \pm 14$ ,  $103 \pm 4$ ,  $106 \pm 8$ , and  $111 \pm 7\%$ , respectively (Clauss et al. 1994; Ligotke et al. 1994).

**A.4.3 Gravimetric Results.** Gravimetric results yield water vapor concentrations. This is because the total mass concentration of other vapors in the headspaces of Hanford waste tanks, measured in  $\mu\text{g}/\text{L}$ , are typically two or three orders of magnitude less than the  $\text{mg}/\text{L}$  mass concentrations of the water vapor found in even relatively dry tanks. The water vapor mass concentration collected in the 5-trap sorbent trains was  $8.9 \pm 0.3 \text{ mg}/\text{L}$ , based on dry air sample volumes ( $0^\circ\text{C}$  and 760 torr). The result was determined from an average mass gain of 17.4 mg from all four sample trains. The blank correction applied to the results was 0.35 mg per train, based on a mass loss of  $0.35 \pm 0.05$  mg per two 5-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of  $\pm 0.1$  mg. Although no spiked blanks were tested, the percentage recovery of mass from three blank  $\text{H}_2\text{O}$  traps spiked with 51 mg water was  $103 \pm 2\%$  during a previous sample job (Clauss et al. 1994).

Corrected for a measured tank headspace temperature of  $15.2^\circ\text{C}$  and pressure of 748.1 torr, the actual water vapor mass concentration from the gravimetric results was  $8.2 \pm 0.3 \text{ mg}/\text{L}$ . Also based on analytical results, the partial pressure of water vapor was  $8.1 \pm 0.4$  torr, the relative humidity was  $63 \pm 2\%$ , and the dew point was  $8.3 \pm 0.3^\circ\text{C}$ .

**Table A.2** List of PNNL Inorganic Samples, Controls, and Gravimetric Results Obtained from a Heated Tube Inserted into the Headspace of Tank BX-110 on 4/30/96

Sample Number	Sorbent Train Type	Sample Port and Volume Information <sup>(a)</sup>				
		Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
<u>Samples:</u>						
S6046-A07-S67	NH3/NO2/H2O	1	200.0	10.0	2.00	0.0175
S6046-A08-S68	NH3/NOx/H2O	2	200.0	10.0	2.00	0.0172
S6046-A09-S69	NH3/NOx/H2O	3	200.0	10.0	2.00	0.0181
S6046-A10-S70	NH3/H2O/H2O	4	200.0	10.0	2.00	0.0167
<u>Controls:</u>						
S6046-A15-S71	NH3/NOx/H2O Field Blank	n/a <sup>(b)</sup>	n/a	n/a	n/a	-0.0004
S6046-A16-S72	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	-0.0003

(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.

**Table A.3** Inorganic Vapor Sample Results Obtained from a Heated Tube Inserted into the Headspace of Tank BX-110 on 4/30/96

Sample	Analytical Results ( $\mu\text{mol}$ )			Sample Volume (L)	Vapor <sup>(a)</sup> Concentration (ppmv)
	Front Section	Back Section	Total <sup>(b)</sup> Blank-Corrected		
<u>NH<sub>3</sub> Samples:</u>			<u>5.63</u>	<u>2.00</u>	<u>63 ± 3</u>
S6046-A07-S67	5.30	0.048	5.21	2.00	58.3
S6046-A08-S68	5.81	NA <sup>(c)</sup>	5.72	2.00	64.0
S6046-A09-S69	5.95	NA	5.86	2.00	65.6
S6046-A10-S70	5.85	0.056	5.76	2.00	64.5
<u>NO<sub>2</sub> Samples:</u>			<u>&lt;0.013</u>	<u>2.00</u>	<u>&lt;0.15</u>
S6046-A07-S67	0.0130	0.0070	<0.013	2.00	<0.15
S6046-A08-S68	0.0102	NA	<0.013	2.00	<0.15
S6046-A09-S69	0.0115	0.0057	<0.013	2.00	<0.15
S6046-A10-S70	0.0100	NA	<0.013	2.00	<0.15
<u>NO Samples:</u>			<u>&lt;0.013</u>	<u>2.00</u>	<u>&lt;0.15</u>
S6046-A07-S67	0.0106	NA	<0.013	2.00	<0.15
S6046-A08-S68	0.0102	0.0054	<0.013	2.00	<0.15
S6046-A09-S69	0.0104	NA	<0.013	2.00	<0.15
S6046-A10-S70	0.0106	0.0057	<0.013	2.00	<0.15
<u>Gravimetric Samples:</u>			<u>17.7 mg</u>	<u>2.00</u>	<u>8.9 ± 0.3 mg/L</u>
S6046-A07-S67	n/a <sup>(c)</sup>	n/a	17.9	2.00	8.9
S6046-A08-S68	n/a	n/a	17.6	2.00	8.8
S6046-A09-S69	n/a	n/a	18.5	2.00	9.2
S6046-A10-S70	n/a	n/a	17.1	2.00	8.5

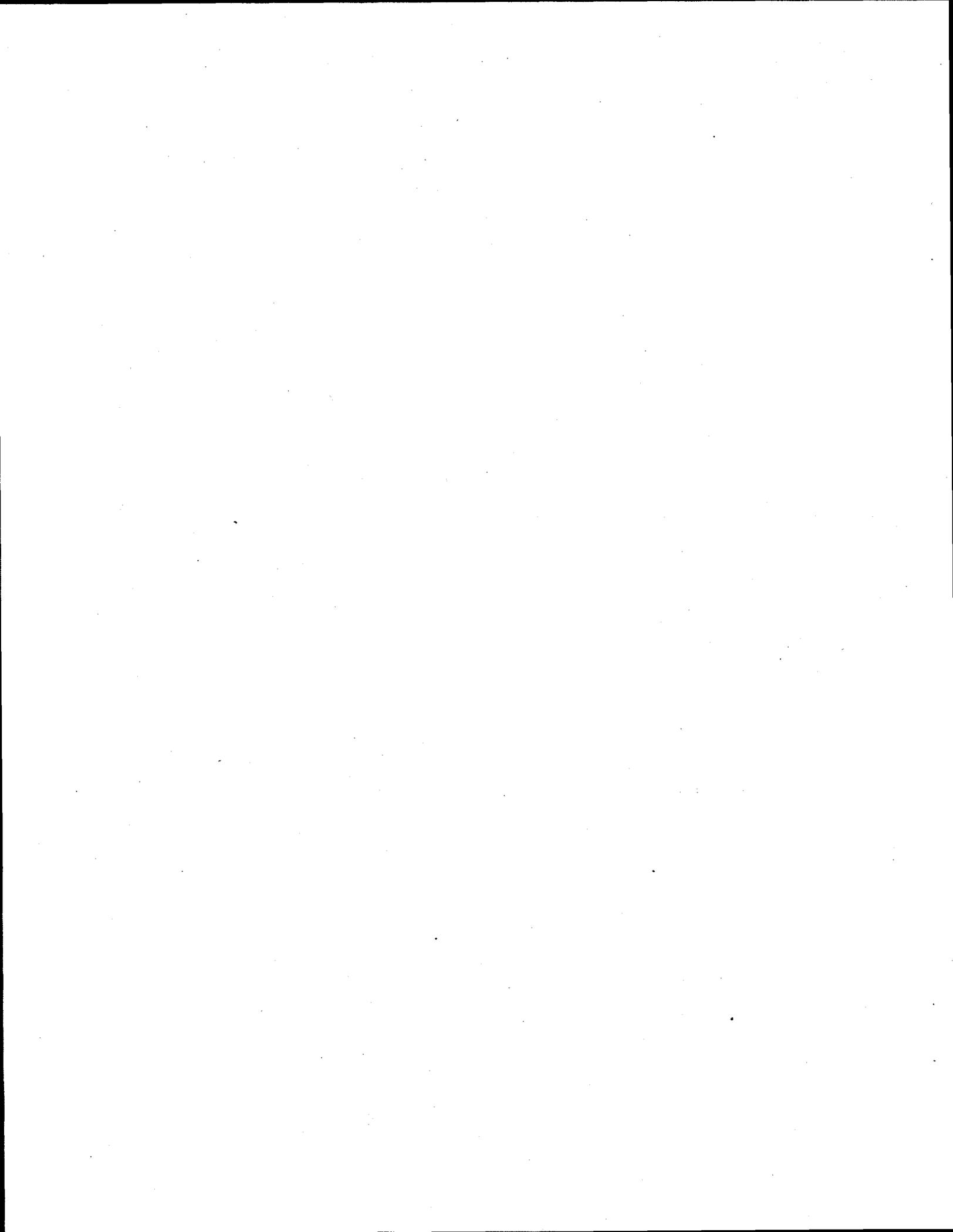
- (a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (Table A.2). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrite. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks. Underlined values represent the average of the set of samples. Concentration uncertainty equals  $\pm 1$  standard deviation (absolute) for each set of samples. Percentage RSD may be determined by dividing standard deviation by the average and multiplying the result by 100. The use of "<" is defined in Section A.4.
- (b) 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.
- (c) NA = not analyzed; n/a = not applicable.

## 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 National 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 National Laboratory, Richland, Washington.

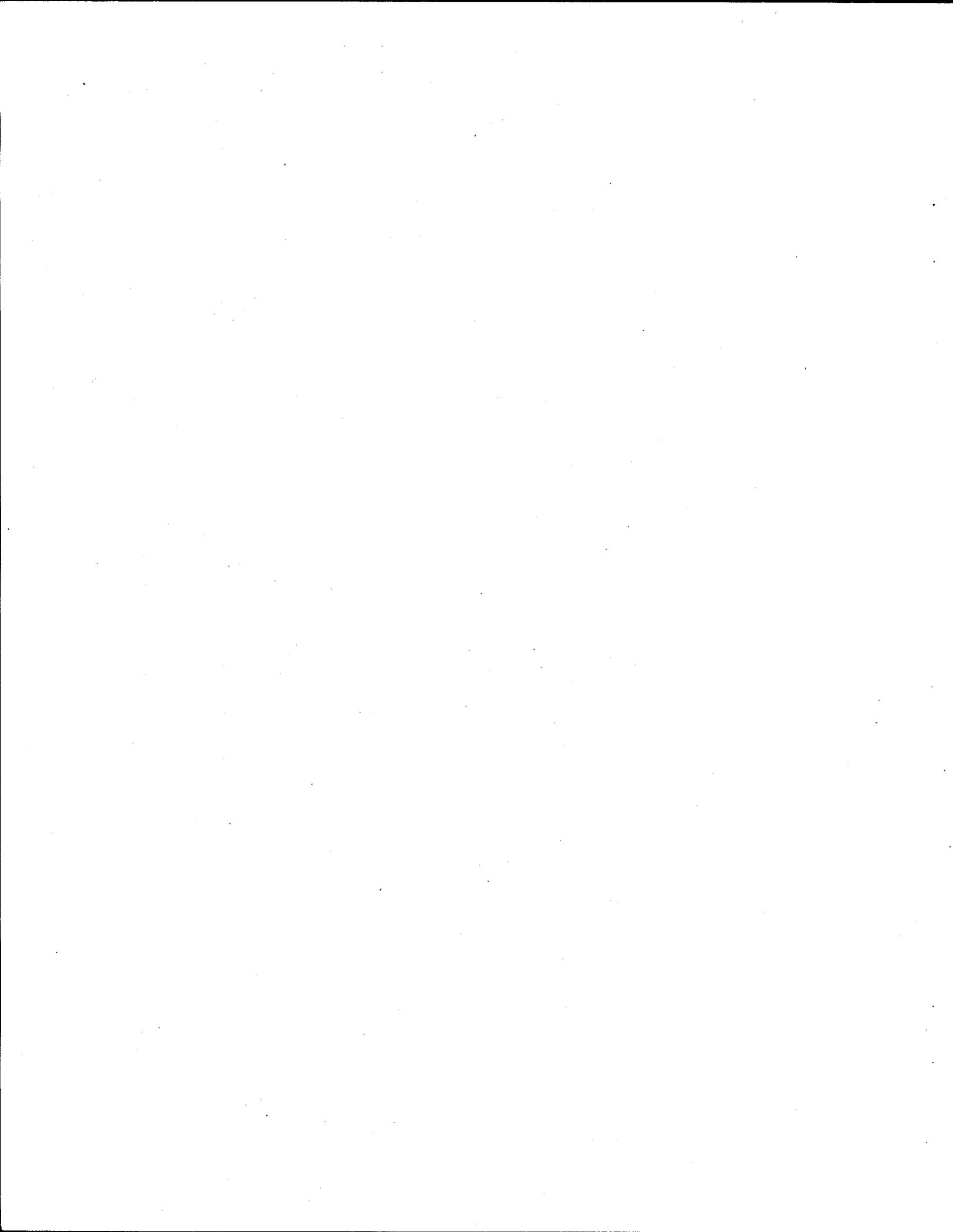
Osborne, J. W., J. L. Huckaby, E. R. Hewitt, C. M. Anderson, D. D. Mahlum, B. A. Pulsipher, and J. Y. Young. 1995. *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Resolution*. WHC-SD-WM-DQO-002, Rev. 1, Westinghouse Hanford Company, Richland, Washington.



## **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. If the canister is verified as clean by TO-12, 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.

#### B.2 Analytical Procedure

The SUMMA™ canister samples were analyzed for permanent gases according to PNNL Technical Procedure PNL-TVP-05<sup>(b)</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 ( $H_2$ ), carbon dioxide ( $CO_2$ ), carbon monoxide (CO), methane ( $CH_4$ ), and nitrous oxide ( $N_2O$ ), by gas chromatograph/thermal conductivity detection (GC/TCD). Aliquots of sampled air are drawn directly from each canister into a 5-mL gas-tight syringe and injected into a Hewlett-Packard 5890 GC/TCD fitted with a loop injector valve and a column switching valve. An aliquot of 5 mL is used so that the 1.0-mL injection loop is completely purged with sample air, ensuring that no dilution of the sample takes place within the injection loop. One set of GC conditions is used to analyze for CO,  $CO_2$ ,  $N_2O$ , and  $CH_4$  using Helium (He) as the carrier gas. A second GC analysis is performed for  $H_2$  (using nitrogen as the carrier gas) to enhance the signal sensitivity and lower the detection limit for this analyte. The permanent gases and associated EQLs 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, Pacific Northwest Laboratory, Richland, Washington.

(b) Pacific Northwest Laboratory. 5/96. *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. 2). PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

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

<u>Analyte</u>	<u>Formula</u>	<u>Procedure</u>	<u>Estimated Quantitation Limit (ppmv)</u>
Carbon Dioxide	CO <sub>2</sub>	PNL-TVP-05	17
Carbon Monoxide	CO	PNL-TVP-05	17
Methane	CH <sub>4</sub>	PNL-TVP-05	25
Hydrogen	H <sub>2</sub>	PNL-TVP-05	17
Nitrous Oxide	N <sub>2</sub> O	PNL-TVP-05	17

### **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 CH<sub>4</sub> over a range of 25 to 2100 parts per million by volume (ppmv) and for CO, CO<sub>2</sub>, and N<sub>2</sub>O over a range of 17 to 2100 ppmv using standards at five different concentrations and He as a carrier gas. A similar procedure was followed for H<sub>2</sub> with a range of 17 to 2120 ppmv, except the carrier gas was changed to N<sub>2</sub>. An average response factor from the calculation was used for quantification of compound peak area.

Each analyte was quantitated by comparison of sample analyte peak area to the calibration plot generated for the compound. The estimated quantitation limit (EQL) for the method has been established as the low level calibration standard. 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 ~10 m upwind of Tank BX-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 BX-110, ambient air collected ~10 m upwind of the tank, and ambient air collected through the VSS. Samples were analyzed on June 6 and 10, 1996. No permanent gases were observed above the EQL in the tank headspace samples. A replicate analysis was performed on SUMMA™ PNL 213; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

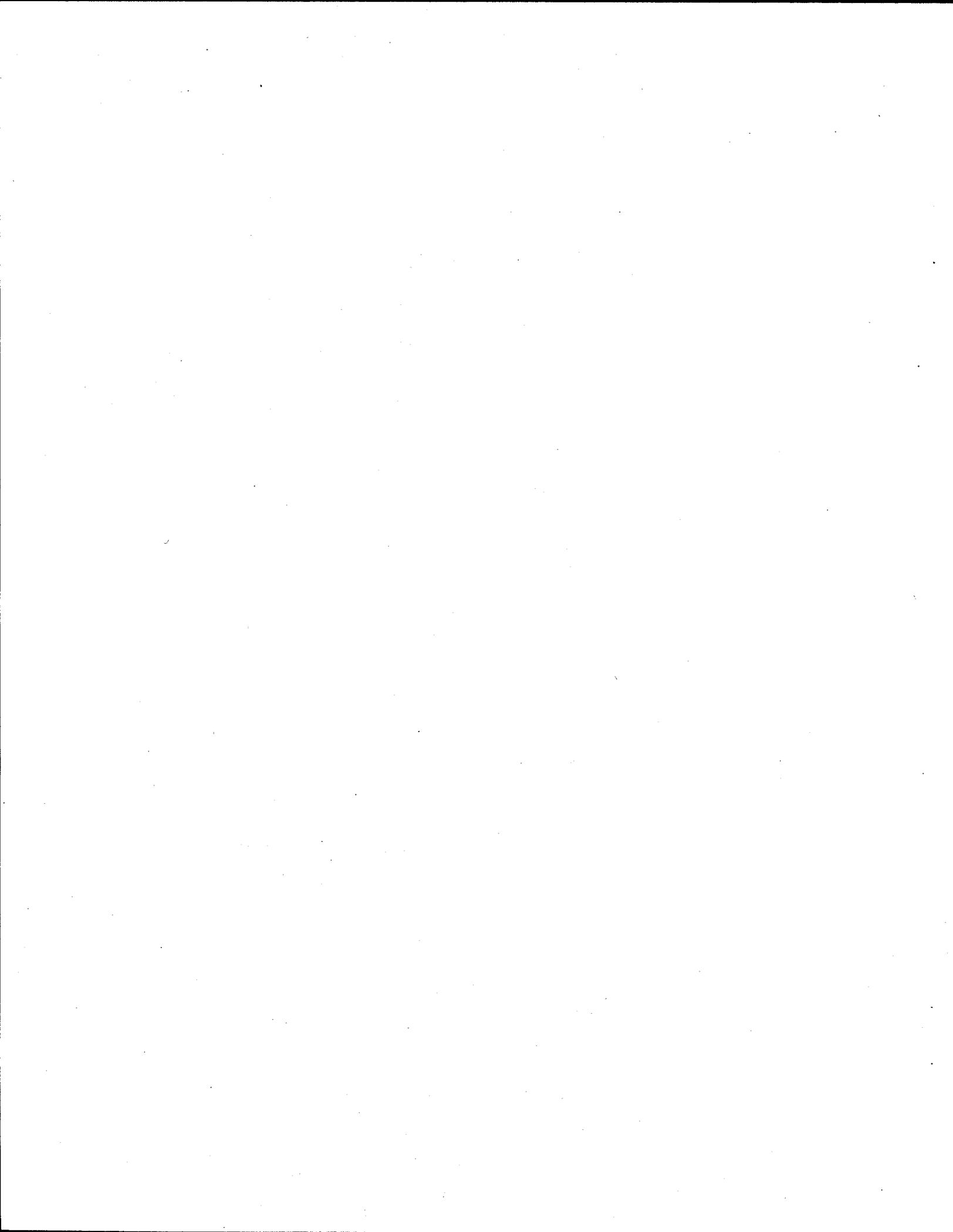
**Table B.2** Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank BX-110 and for Ambient Air and Ambient Air Through the VSS Collected near Tank BX-110 in SUMMA (TM) Canisters on 4/30/96

Permanent Gas Analyte	Ambient Air Upwind		Ambient Air Through VSS		Tank Samples				Average Concentration Tank Samples (ppmv)			
	S6046-A01.115 <sup>(a)</sup> PNL 115 <sup>(b)</sup> Concentration (ppmv)	<17 <25 377 <17 <17	S6046-A02.121 <sup>(a)</sup> PNL 121 <sup>(b)</sup> Concentration (ppmv)	<17 <25 378 <17 <17	S6046-A04.155 <sup>(a)</sup> PNL 155 <sup>(b)</sup> Concentration (ppmv)	<17 <25 <17 <17 <17	S6046-A05.213 <sup>(a)</sup> PNL 213 <sup>(b)</sup> Concentration (ppmv)	<17 <25 <17 <17 <17		S6046-A06.255 <sup>(a)</sup> PNL255 <sup>(b)</sup> Concentration (ppmv)	<17 <25 <17 <17 <17	S6046-A05.213 <sup>(c)</sup> PNL 213 <sup>(b)</sup> Concentration (ppmv)
Hydrogen												
Methane												
Carbon Dioxide												
Carbon Monoxide												
Nitrous Oxide												

(a) WHC sample identification number.

(b) PNL canister number.

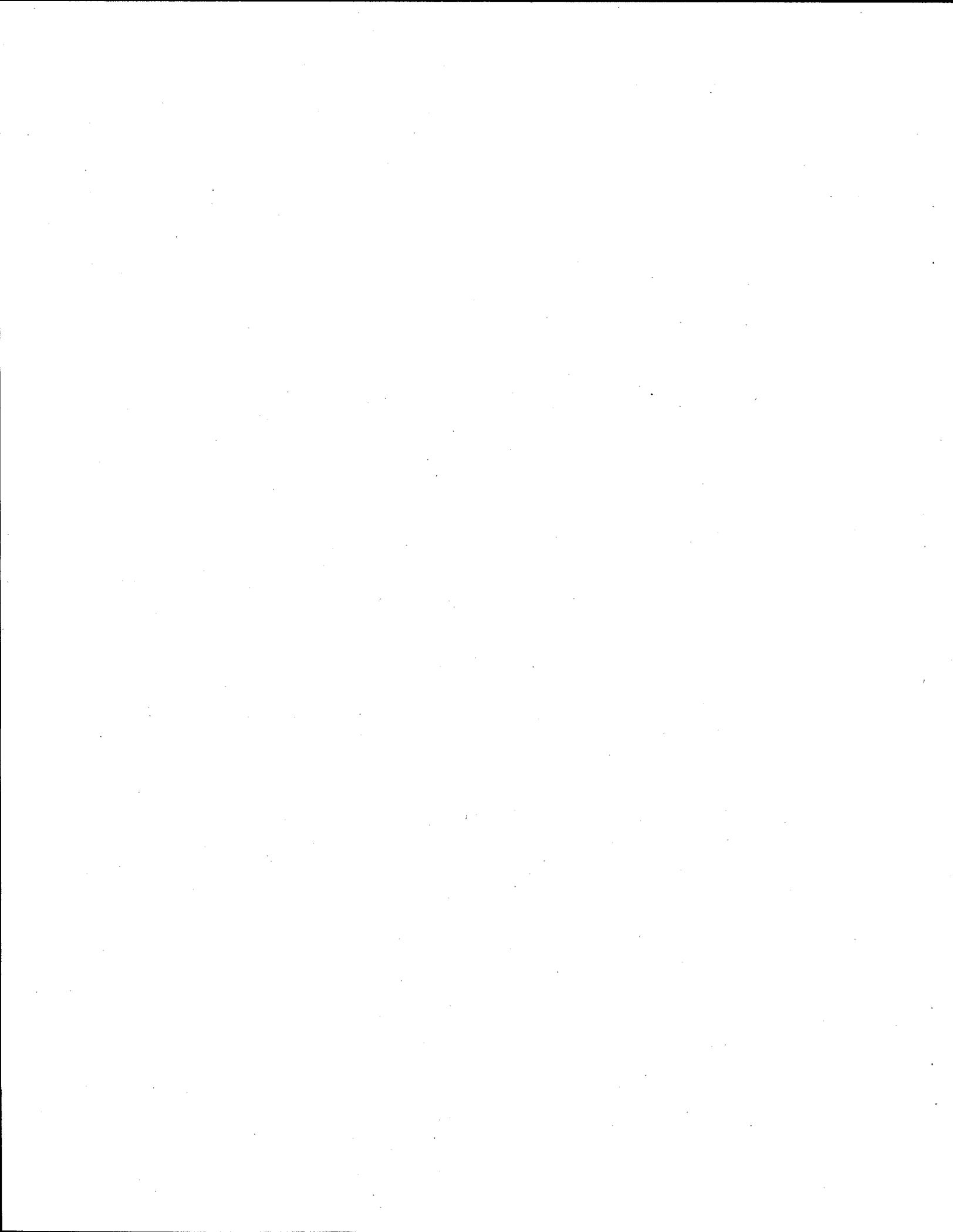
(c) Replicate analysis for PNL 213; results are not included in the calculation of average concentrations.



## **Appendix C**

### **Tank Vapor Characterization:**

### **Total Non-Methane Organic Compounds**



## Appendix C

### Tank Vapor Characterization: Total Non-Methane Organic Compounds

#### 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. If the canister is verified as clean by TO-12, the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 µL of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

#### C.2 Analytical Procedure

The SUMMA™ canister samples were analyzed according to PNNL Technical Procedure PNL-TVP-08<sup>(b)</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 non-methane 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.

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.

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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, Pacific Northwest Laboratory, Richland, Washington.

(b) Pacific Northwest Laboratory. 12/95. *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. 1), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

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 QA plan ETD-002.

The TNMOC is calibrated by using propane as the calibration standard. 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 continuing calibration verification (CCV) standard of 100 ppmv propane is analyzed to confirm acceptability of instrument performance. The initial calibration is then 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 is 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 Organic Compounds Sample Results

Table C.2 lists results of the TO-12 gas analysis from samples collected from the headspace of Tank BX-110, ambient air collected ~10 m upwind of the tank, and ambient air collected through the VSS. Samples were analyzed on July 31, 1996. Concentrations in the ambient air samples ranged from 0.69 mg/m<sup>3</sup> to 0.74 mg/m<sup>3</sup>. Concentrations in the three tank headspace samples ranged from 1.84 mg/m<sup>3</sup> to 2.13 mg/m<sup>3</sup> with an average concentration of 1.96 mg/m<sup>3</sup>. This compares to 3.76 mg/m<sup>3</sup> for the sum of all compounds identified in the target and TIC analysis of the SUMMA™ canisters.

**Table C.1** TO-12 Results for Samples Collected from the Headspace of Tank BX-110 and for Ambient Air and Ambient Air Through the VSS Collected near Tank BX-110 in SUMMA (TM) Canisters on 4/30/96.

TO-12	Ambient Air		Ambient Air Through VSS		Tank Samples				Average Concentration Tank Samples (mg/m3)	
	Upwind	Concentration (mg/m3)	PNL 115 <sup>(b)</sup>	Concentration (mg/m3)	S6046-A01.115 <sup>(a)</sup>	PNL 115 <sup>(b)</sup>	S6046-A04.155 <sup>(a)</sup>	PNL 155 <sup>(b)</sup>		S6046-A05.213 <sup>(a)</sup>
	0.74	J	0.69	J	2.13	1.92	1.84	1.92	1.96	

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 213; results are not included in the calculation of average concentrations.

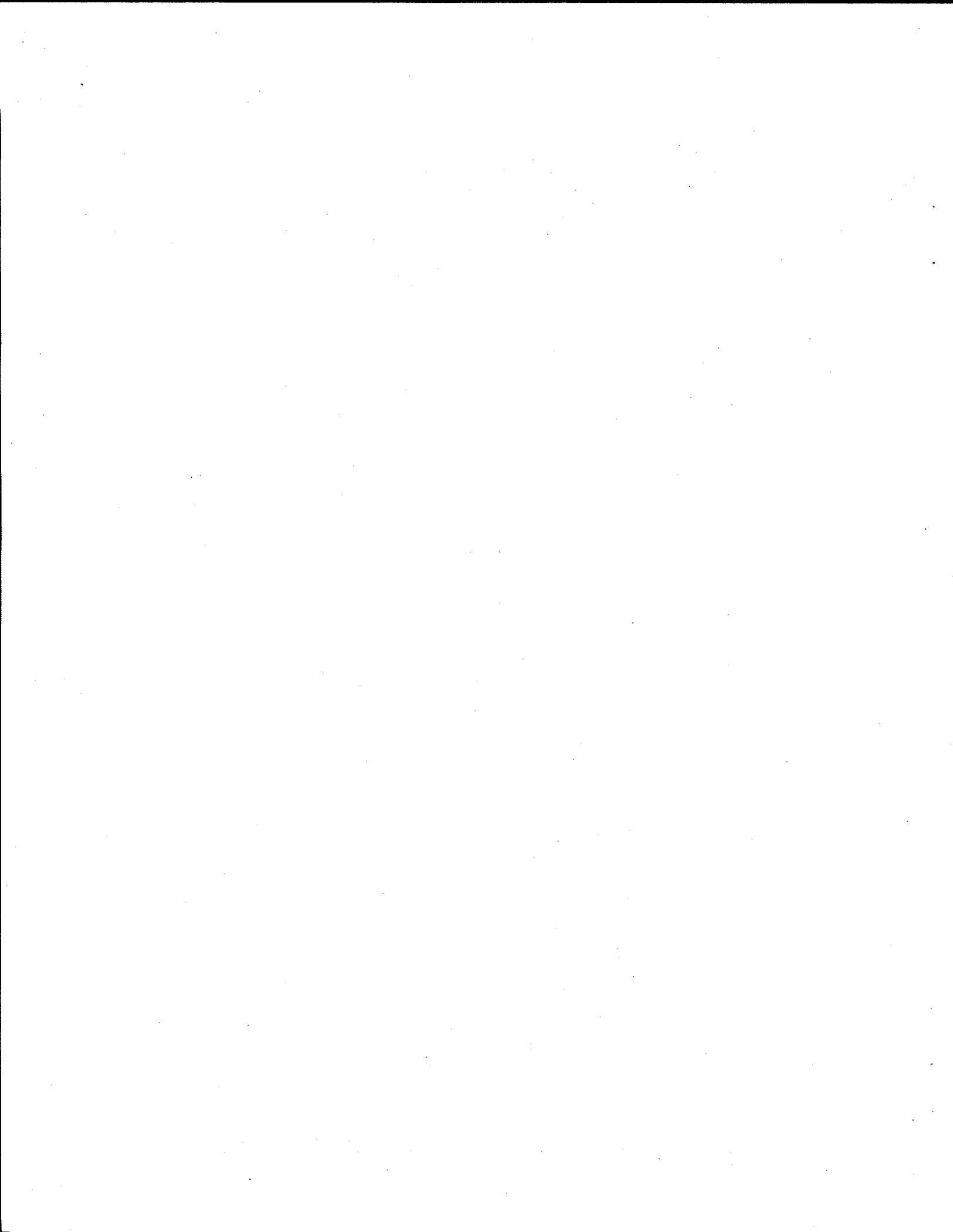
Data Qualifier Flags

J Result above the IDL but below the EQL.

## **Appendix D**

**Tank Vapor Characterization:**

**Organic Analytes by SUMMA™ Method**



## Appendix D

### Tank Vapor Characterization: Organic Analytes by SUMMA™ Method

#### 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 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. 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>(b)</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 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.

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<sup>(a)</sup> 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.

<sup>(b)</sup> Pacific Northwest Laboratory. 8/96. *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. 2), PNL Technical Procedure, Richland, Washington.

The instrument calibration mixture for the PNL-TVP-03 analysis consists of 66 organic analytes. These 66 compounds that are directly quantified in this analysis make up the target analyte list (these 66 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

**Table D.1** Target Organic Analytes

Dichlorodifluoromethane	p/m-Xylene
Chloromethane	1-Pentanenitrile
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	Nonane
Undecane	Dodecane
Tridecane	Tetradecane
Butane	Pentane
1-Butanol	Octane
1-Hexanenitrile	1-Ethyl-2-methylbenzene
Methanol <sup>(a)</sup>	Ethanol <sup>(a)</sup>

(a) The low level standard is used as the EQL for these compounds

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 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. Instrument detection limits and EQLs for the target analytes have been developed.

### 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 66 organic compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d<sub>5</sub>, and bromofluorobenzene was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank headspace samples are analyzed.

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

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

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

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<sup>(a)</sup> Pacific Northwest Laboratory. 11/94. *Preparation of TO-14 Volatile Organic Compounds Gas Standards*, PNL-TVP-06 (Rev. 0). PNL Technical Procedure, Richland, Washington.

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

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

#### D.4 Volatile Organic Sample Results

Five SUMMA™ canisters were returned to the laboratory on May 15 under WHC COC form 100078 (see Appendix F). Samples were analyzed on July 11 and 12, 1996.

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 BX-110 and through the VSS near Tank BX-110 are presented in Table D.4.

Table D.2 lists the quantitative results for compounds listed as target analytes and TICs. Twenty-two target analytes above the IDL and two TICs were detected in the tank headspace samples. Seventeen target analytes and one TIC were identified in two or more tank headspace samples. Ethanol at 1.53 mg/m<sup>3</sup> and methanol at 1.37 mg/m<sup>3</sup> accounted for 77% of the compounds identified in the analysis. The total concentration of the target analytes was found to be 3.75 mg/m<sup>3</sup>. The only TIC specifically identified in these samples was butanal (0.16 mg/m<sup>3</sup>). The total concentration of all the compounds identified was 3.76 mg/m<sup>3</sup>. This compares to a total concentration of 1.96 mg/m<sup>3</sup> identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 213 was analyzed in replicate for target analytes and TICs to determine analytical precision. The RPD results are presented in Table D.3. The RPDs were calculated for analytes detected above the IDL and found in both replicates. Six of 15 compounds had RPDs of less than 10%.

Table D.4 lists the quantitative results for compounds listed as target analytes and TICs in ambient air and ambient air through the VSS. Twelve compounds were observed in one or both of the ambient air samples. Acetone at 15 ppbv and cyclohexane at 21 ppbv were observed in the upwind ambient air sample.

The following procedural changes and observations were noted during the analysis of Tank BX-110:

Three target compounds (pyridine at 79.3%, tridecane at 38.7%, and tetradecane at 51.5%) surpassed the 30% relative standard deviation (% RSD) acceptance criteria for the initial calibration. Pyridine was found in tank samples S6046-A01.115, S6046-A02.121 and S6046-A04.155 in concentrations between IDL and EQL. Pyridine was also found in the continuing calibration blank (CCB) in concentration between IDL and EQL; therefore, one can assume that this substance present in the tank samples is due to crossover contamination of the device. Tridecane and tetradecane were not found in the tank samples in concentrations above IDL.

Two target compounds (pyridine and tetradecane) were outside the 25% difference (% D) acceptance criteria for the CCV sample; however, the CCV passed the procedural criterion requiring +25% D passage for 85% of all target compounds. Tetradecane was not found in tank samples in concentrations above IDL. Pyridine was found in several tank samples as noted above. No target compounds were found in the CCB above the EQL.

The compound 1,2,4-trichlorobenzene was detected in the initial calibration blank above the EQL; however, it was not found in the CCB or tank samples.

The internal standard quantification area percent recovery for the last tank sample (S6046-A06.255) and blank exceeded the acceptance criterion (50% < quantification < 200%) allowed by procedure PNL-TVP-03, Rev. 1. The changes in the internal standard areas was caused by water induced fatigue. This problem is routinely observed with the HP5972 GC/MS system because of its poor pumping capacity, the high water and ammonia content in these samples. Target compounds found in these samples could be affected. This problem will continue until a larger GC/MS system is used in the analysis.

Methanol and ethanol are not currently included in the method performance section for System 1; however, both analytes were analyzed by this method. The low level standard is used as the EQL for these compounds. Sample results are flagged with a less-than symbol (<) when less than the EQL value.

**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 BX-110 in SUMMA™ Canisters collected on 4/30/96

Target Analytes <sup>(a)</sup>	CAS	MW	Ret Time	S6046-A04.155 <sup>(c)</sup>		S6046-A05.213 <sup>(c)(d)</sup>		S6046-A06.255 <sup>(c)</sup>		Mean and Standard Deviation						
				(mg/m <sup>3</sup> )	(ppbv)	(mg/m <sup>3</sup> )	(ppbv)	(mg/m <sup>3</sup> )	(ppbv)	(mg/m <sup>3</sup> )	St. Dev (ppbv)	St. Dev				
Dichlorodifluoromethane	75-71-8	121	4.6	0.007	1.2	J	0.006	1.1	J	0.008	1.4	J	0.007	0.001	1.3	0.1
Methanol	67-56-1	32	5.2	1.229	859	Y	1.446	1011	Y	1.431	1000	Y	1.369	0.121	957	85
Butane	106-97-8	58	5.9	0.008	3.2	J	0.007	2.8	J	0.011	4.3	J	0.009	0.002	3.4	0.7
Ethanol	64-17-5	46	6.8	1.499	730	Y	1.467	714	Y	1.623	790	Y	1.530	0.082	745	40.1
Acetonitrile	75-05-8	41	7.3	0.006	3.3	J	0.009	4.9	J	0.010	5.7	J	0.009	0.002	4.6	1.2
Acetone	67-64-1	58	7.8	0.433	167		0.499	193		0.530	204		0.487	0.050	188	19
Trichlorofluoromethane	75-69-4	137	8.2	0.034	5.5	J	0.030	4.9	J	0.040	6.6	J	0.035	0.005	5.6	0.9
Pentane	109-66-0	72	8.9	0.004	1.2	U	0.008	2.4	J	0.010	3.0	J	0.009	e	2.7	e
Methylene Chloride	75-09-2	85	9.7	0.020	5.2	J	0.018	4.7	J	0.021	5.5		0.019	0.001	5.1	0.4
Propanol	71-23-8	60	10.9	0.044	16		0.050	18		0.051	19		0.048	0.004	18	1.3
Propanenitrile	107-12-0	55	10.9	0.004	1.6	U	0.004	1.6	U	0.004	1.6	J	e	e	e	e
2-Butanone	78-93-3	72	12.5	0.024	7.4	J	0.025	7.8	J	0.023	7.1	J	0.024	0.001	7.4	0.3
Tetrahydrofuran	109-99-9	72	14.6	0.005	1.5	J	0.005	1.4	J	0.006	2.0	J	0.005	0.001	1.6	0.3
1-Butanol	71-36-3	74	16.3	0.094	28		0.099	30		0.112	34		0.101	0.009	30.6	2.9
Benzene	71-43-2	78	16.7	0.002	0.49	J	0.002	0.5	U	0.002	0.6	J	0.002	e	0.54	e
Cyclohexane	110-82-7	84	17.3	0.077	20		0.077	20		0.004	1.0	U	0.077	e	20	e
Heptane	142-82-5	100	19.3	0.002	0.4	U	0.002	0.4	U	0.002	0.5	J	e	e	e	e
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.004	0.8	J	0.004	0.9	J	0.004	0.8	J	0.004	0.000	0.83	0.1
Pyridine	110-86-1	79	20.6	0.020	5.7	J	0.019	5.3	U	0.019	5.3	U	e	e	e	e
Toluene	108-88-3	92	22.6	0.011	2.8	J	0.007	1.7	J	0.015	3.7	J	0.011	0.004	2.7	1.0
Tetrachloroethylene	127-18-4	166	25.2	0.004	0.6	U	0.004	0.6	U	0.004	0.6	J	e	e	e	e
Hexanenitrile	628-73-9	97	27.0	0.007	1.5	J	0.005	1.2	U	0.005	1.2	U	e	e	e	e

**Tentatively Identified Compounds<sup>(b)</sup>**

Unknown Alcohol			9.5	0.013	f		nd	nd		nd	nd		e	e	e	e
Butanal	123-72-8	72	12.3	0.015	4.6	N	0.011	3.3	N	nd	nd		0.013	e	3.9	e

**Data Quality Flags**

J Target compound detected above the IDL but below the EQL.

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

Y Initial calibration and CCV was performed; however, the analyte was not part of the current operating procedure.

**Footnotes**

- (a) TO-14 plus 26 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) Mean and/or standard deviation are not meaningful for this analyte.
- (f) No molecular weight available for calculation.

nd Not Detected

**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 BX-110 on 4/30/96**

Target Analytes <sup>(a)</sup>	CAS	MW	Ret Time	S6046-A05.213 <sup>(c)</sup>			S6046-A05.213 <sup>(c)</sup>			Relative Percent Difference <sup>(d)</sup>
				(mg/m <sup>3</sup> )	(ppbv)	Flag	(mg/m <sup>3</sup> )	(ppbv)	Flag	%
Dichlorodifluoromethane	75-71-8	121	4.6	0.006	1.1	J	0.007	1.3	J	14
Chloromethane	74-87-3	50	4.9	0.002	1.1	U	0.002	1.1	J	
Methanol	67-56-1	32	5.2	1.446	1011	Y	1.405	982	Y	3
Butane	106-97-8	58	5.9	0.007	2.8	J	0.008	3.1	J	9
Ethanol	64-17-5	46	6.8	1.467	714	Y	1.632	795	Y	11
Acetonitrile	75-05-8	41	7.3	0.009	4.9	J	0.010	5.7	J	14
Acetone	67-64-1	58	7.8	0.499	193		0.495	191		1
Trichlorofluoromethane	75-69-4	137	8.2	0.030	4.9	J	0.039	6.3	J	25
Pentane	109-66-0	72	8.9	0.008	2.4	J	0.008	2.5	J	2
Methylene Chloride	75-09-2	85	9.7	0.018	4.7	J	0.020	5.3	J	11
Propanol	71-23-8	60	10.9	0.050	18		0.052	19		4
2-Butanone	78-93-3	72	12.5	0.025	7.8	J	0.023	7.3	J	7
Tetrahydrofuran	109-99-9	72	14.6	0.005	1.4	J	0.006	1.8	J	25
1-Butanol	71-36-3	74	16.3	0.099	30		0.089	27		11
Benzene	71-43-2	78	16.7	0.002	0.46	U	0.003	0.71	J	
Cyclohexane	110-82-7	84	17.3	0.077	20		0.004	1.0	U	
Heptane	142-82-5	100	19.3	0.002	0.40	U	0.002	0.54	J	
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.004	0.92	J	0.005	1.1	J	14
Toluene	108-88-3	92	22.6	0.007	1.7	J	0.015	3.6	J	73

**Tentatively Identified Compounds<sup>(b)</sup>**

Butanal	123-72-8	72	12.3	0.011	3.3	N	nd	nd		
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**Data Quality Flags**

J Target compound detected above the IDL but below the EQL.

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

Y Initial calibration and CCV was performed; however, the analyte was not part of the current operating procedure.

**Footnotes**

(a) TO-14 plus 26 additional target analytes.

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

(c) WHC sample identification number.

(d) Relative percent difference based on mg/m<sup>3</sup> values

nd Not Detected

**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 BX-110 in SUMMA<sup>TM</sup> Canisters on 4/30/96

Target Analytes <sup>(a)</sup>	CAS	MW	Ret Time	Upwind Ambient S6046-A01.115 <sup>(c)</sup>			Upwind Ambient Thru VSS S6046-A02.121 <sup>(c)</sup>		
				(mg/m <sup>3</sup> )	(ppbv)	Flag	(mg/m <sup>3</sup> )	(ppbv)	Flag
Dichlorodifluoromethane	75-71-8	121	4.6	0.003	0.63	J	0.005	0.84	J
Acetone	67-64-1	58	7.8	0.040	15		0.011	4.3	J
Methylene Chloride	75-09-2	85	9.7	0.015	4.0	J	0.017	4.4	J
Propanol	71-23-8	60	10.9	0.005	1.8	J	0.004	1.3	J
2-Butanone	78-93-3	72	12.5	0.007	2.2	J	0.004	1.3	J
1-Butanol	71-36-3	74	16.3	0.013	3.9	J	0.006	1.9	J
Cyclohexane	110-82-7	84	17.3	0.078	21		0.004	1.0	U
Pyridine	110-86-1	79	20.6	0.037	11	J	0.019	5.4	J
Hexanenitrile	628-73-9	97	27.0	0.005	1.2	U	0.010	2.3	J
<b>Tentatively Identified Compounds<sup>(b)</sup></b>									
Unknown			4.4	0.008	d		nd	nd	
Acetaldehyde	75-07-0	44	5.2	0.083	42	N	0.029	14	N
Unknown			10.4	nd	nd		0.006	d	

**Data Quality Flags**

J Flag denotes target compound detected above Instrument Detection Limit (IDL), but below Estimated Quantitation Limit (EQL)

N Flag denotes tentatively identified compound

U Flag denotes compound not detected above listed IDL

**Footnotes**

- (a) TO-14 plus 26 additional target analytes.
  - (b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
  - (c) WHC sample identification number.
  - (d) No molecular weight available for calculation.
- nd Not Detected

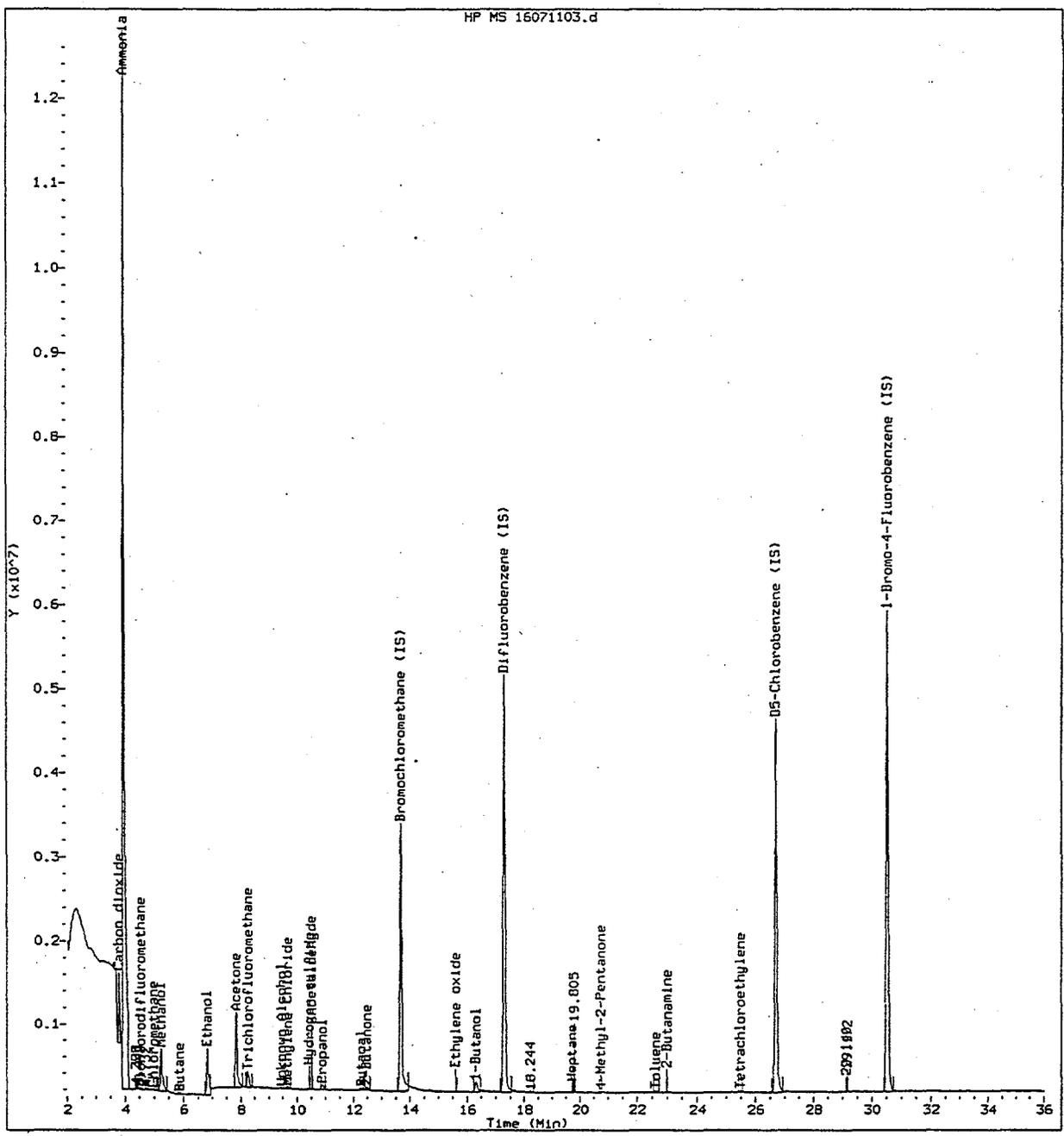
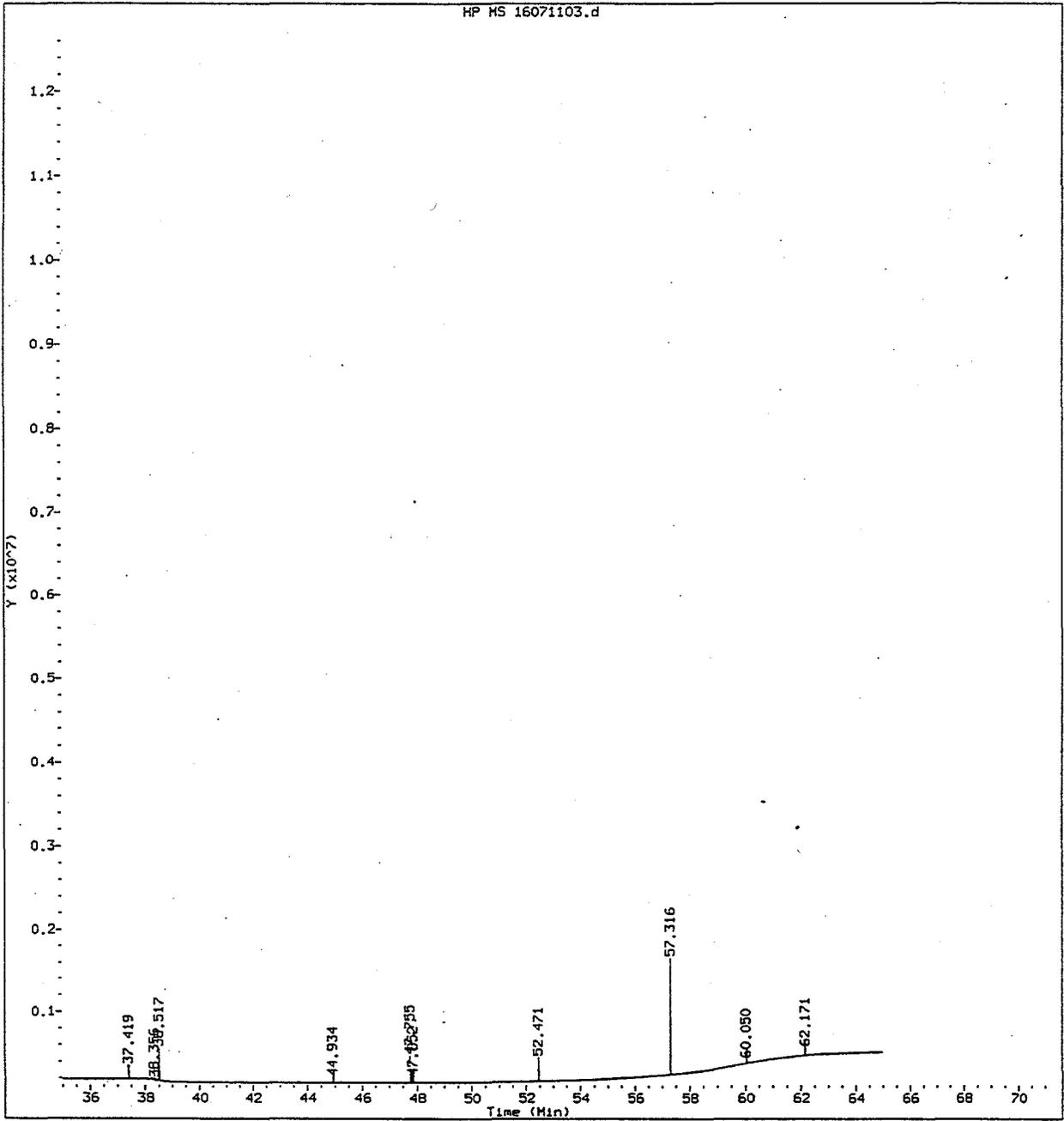


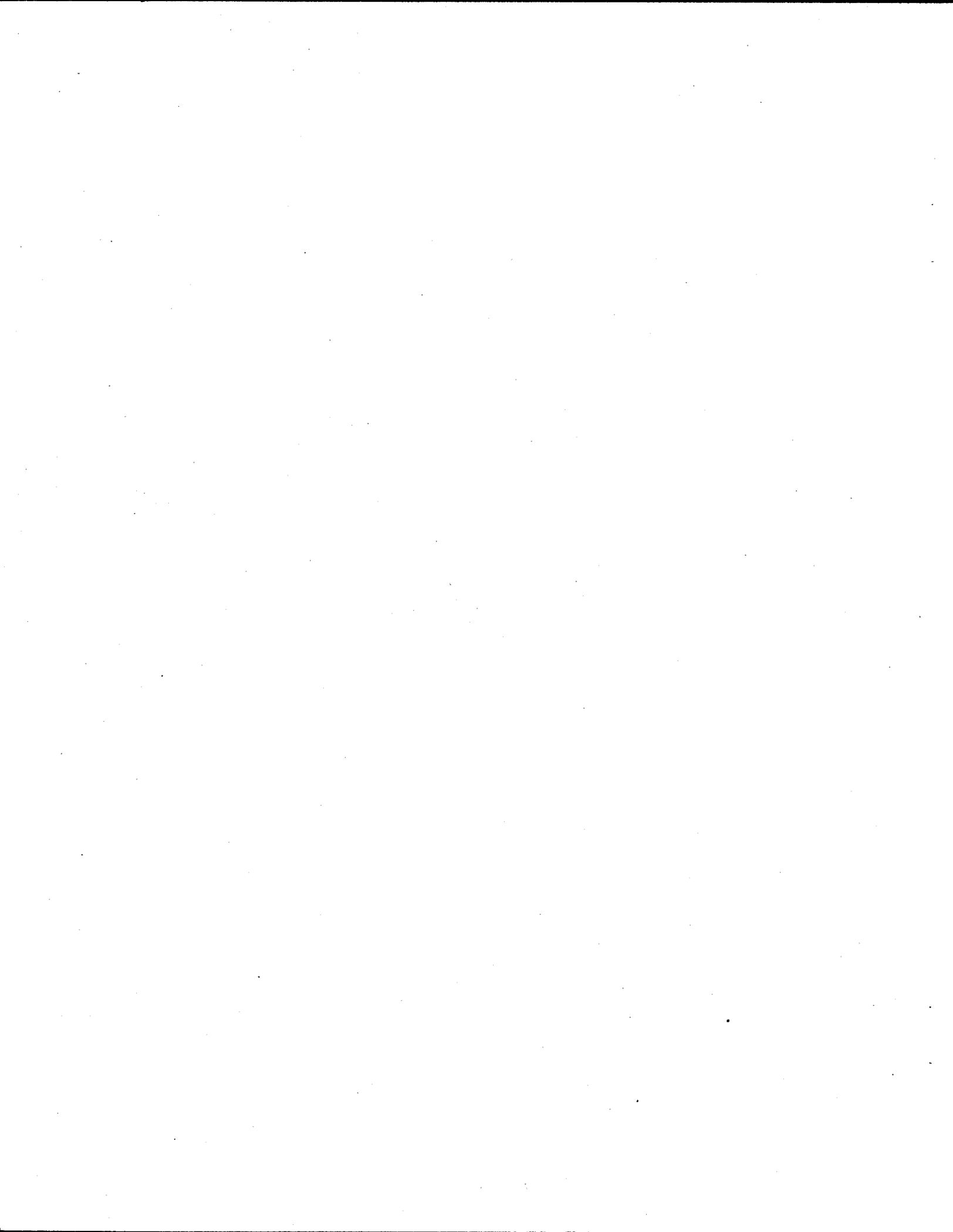
Figure D.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank BX-110 SUMMA™ Canister Sample S6046-A04-155 Collected on 4/30/96



**Figure D.1b** Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank BX-110  
SUMMA™ Canister Sample S6046-A04-155 Collected on 4/30/96

## **Appendix E**

### **Tank Vapor Characterization: Organic Analytes by Triple Sorbent Trap Method**



## Appendix E

### Tank Vapor Characterization: Organic Analytes by Triple Sorbent Trap Method

#### E.1 Sampling Methodology

Samples are collected on Supelco 300 graphite based triple sorbent traps (TST). Before field deployment, each trap is heated to 380°C under inert gas flow for a minimum of 60 min. Tubes are prepared in batches with each tank sampling job constituting one batch. One tube is selected from each batch and run immediately to verify cleanliness. All remaining tubes in the batch receive equal amounts of 3 surrogate compounds (hexafluorobenzene, toluene-d8, and bromobenzene-d5). One per batch tube is run immediately to verify successful addition of surrogate spikes to that batch. Tubes are then placed in individually labeled plastic shipping tubes (Supelco TD<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 2 sorbents are deactivated graphite with limited sorption power for less volatile compounds. The final trapping stage, the Carbosieve™ S-III, is a graphitized molecular sieve used to retain the most volatile components, including some permanent gases such as Freon-12. Following sample collection and addition of internal standard (IS), the traps are transferred to a Dynatherm ACEM 900 thermal desorber unit for analysis. The trap on the ACEM 900 is then desorbed by ballistic heating to 350°C with the sample then transferred to a smaller focusing trap. A 10:1 split is used during the transfer with 10% of the sample analyzed and the rest retained for reanalysis. The split sample collected on a second identical Carbotrap™ 300 trap is used for repeat analysis on at least 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 chromatography (GC) column, which may be thermally desorbed at a helium (He) flow rate compatible with the column and mass spectrometry (MS) interface (1.2 mL/min). The focusing trap is

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(a) Pacific Northwest Laboratory. 2/96. *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. 2), 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 65 compounds. These 65 compounds that are directly quantified in this analysis make up the target analyte list (these 65 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

**Table E.1** Target Organic Analytes

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

(a) The low level standard is used as the EQL for these compounds.

*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.*

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. Instrument detection limits and EQLs for the target analytes have been developed.

### 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 65 compounds shown in Table E.1. A gas mixture containing difluorobenzene, chlorobenzene-d<sub>5</sub>, 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<sup>3</sup> assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

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

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

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

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

The ppbv concentrations are calculated from  $\text{mg/m}^3$  and the molecular weight of the analyte.

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

#### E.4 Organic Sample Results

Ten triple sorbent traps consisting of four samples, two field blanks and two trip blanks were returned to the laboratory on May 15, 1996 under WHC COC form 100079. Samples were analyzed on May 17 and 20, 1996.

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. The analysis of sample S6046-A13.971 was unusable because of an air leak during analysis associated with failure of a Vespel ferrule on the sample inlet tube. Consequently the data for that run was not processed or included in this report.

Table E.2 lists the quantitative results for compounds listed as target analytes and TICs. Seventeen target analytes above the IDL and three TICs were detected in the tank headspace samples. Sixteen of the target analytes and all TICs were observed in two sorbent traps. Methanol ( $0.42 \text{ mg/m}^3$ ) and ethanol ( $0.56 \text{ mg/m}^3$ ) accounted for 57% of the target analytes and 50% of the total concentration identified by the analyses. The total concentration of the target analytes was found to be  $1.72 \text{ mg/m}^3$  or 88% of the total concentration identified by the analyses. The predominant TICs observed in these samples were 1-chloro-1,1-difluoroethane ( $0.17 \text{ mg/m}^3$ ), acetaldehyde ( $0.04 \text{ mg/m}^3$ ), and acetic acid ( $0.04 \text{ mg/m}^3$ ). The total concentration of the TICs was found to be  $0.25 \text{ mg/m}^3$  or 13% of the total concentration identified by analyses. The total concentration of all the compounds identified was  $1.97 \text{ mg/m}^3$ .

Triple sorbent trap sample PNL 970 was analyzed in replicate for target analytes and TICs to determine analytical precision. The RPD results are presented in Table E.3. The RPDs were calculated for analytes detected above the detection limit and found in both replicates. Nine of 16 target analytes had RPDs of less than 10%.

The following procedural changes and observations were noted during the analysis of Tank BX-110:

Methanol and ethanol are not currently included in procedure PNL-TVP-10; however, both compounds were analyzed per this method. The low level standard is used as the EQL for these compounds. Sample results are flagged with a less-than symbol (<) when less than the EQL value.

Tributyl phosphate is included in the target list based on a calibration performed on January 5 and 9, 1996. The TBP was introduced onto a series of double sorbent traps as a methanolic solution standard rather than a vapor standard. This served to determine the retention time and verify the mass spectral characteristics of the compound. However, verification of the calibration acceptability was not performed because the compound is not present in the CCV. At present, it is not possible to prepare a gas standard from this material. The calibration information on TBP demonstrated that detectability at 0.08 ppbv (based on 200 mL sample) was possible. Tributyl phosphate was not detected in the tank samples.

The field and trip blanks contained no target compounds at levels in excess of the EQL. Compounds detected in at least one of the blanks at trace levels (below EQL) included methylene chloride, pyridine, and tetradecane. Field blanks and trip blanks contained minor amounts of 1-chloro-1,1-difluoroethane (TIC). This analyte was also present in the field and trip blanks. This compound has appeared persistently in most samples sent to the field in the past including blanks. It is believed to be a fugitive refrigerant. That material is never present in tubes archived for a similar amount of time in the 326 Vapor Lab or 329 Building temporary storage. The origin of the material is unclear but since it has shown up in trip blanks as well as field blanks, the most likely candidate is one of the refrigerators used for interim storage such as the 222S lab.

The TST samples were analyzed in two batches. The analytical sequence runs (batches) were as follows:

Batch 5/17/96 (file identifier 46051701.d) - S6046-A17.975, S6046-A18.976, S6046-A19.977, S6046-A20.978;

Batch 5/20/96 (file identifier 46052001.d) - S6046-A11.969, S6046-A12.970, S6046-A12.971REP.

The following discussion provides details regarding QC criterion failures for each batch. Batch 5/17/96:

The first CCV run was within nominal limits as specified in the procedure; however, because several compounds typically within the 25% limits were outside that limit, a second CCV was run and used for quantitation. The second CCV was satisfactory for all target compounds except ethanol (31.1%), tridecane (35.6%), and tetradecane (78%). Internal standard (IS) responses were generally acceptable; however, because the IS responses for the CCV were higher than normal, all subsequent IS responses showed a low relative response. Variations in IS response with this method are associated with minor differences in tube packing density which can result in a decrease in split ratio and an increased sensitivity. In this method performance studies including detection limits were run at the highest split ratio (i.e., lowest sensitivity) and data quality is not impacted provided the IS responses for individual samples are not anomalously low in absolute as opposed to relative intensity. In this run, the third internal standard responses for the last two samples were slightly below the nominal minimums (relative to CCV) specified in the procedure. Since the absolute responses for these blank samples were within normal tolerances, the required detectability should be readily obtained. A rerun of the samples was not possible. The CCB contained trace amounts (below EQL) of tetradecane. The CCB was otherwise clean.

Very narrow air spikes (mass 32) occasionally are present in chromatograms from this period. This problem has been traced to high frequency air bursts from the surface of MS vacuum system o-rings. Attempts at permanently eliminating this problems have been unsuccessful to date and the matter has been referred to HP for further investigation. It has no known impact on data quality but the spikes do appear as features on the total ion chromatogram.

Batch 5/20/96:

The first CCV was within nominal limits as specified in the procedure, however, because several compounds typically within the 25% limits were outside that limit, a second CCV was run and used for quantitation. The second CCV was satisfactory for all target compounds except chloromethane (30.8%), methanol (28.1%), ethanol (34.7%), tridecane (26.7%), and tetradecane (69.6%). Absolute IS responses were generally acceptable; however, because the CCV had an unusually high response subsequent runs were somewhat low relative to the CCV. For a more complete discussion see batch 5/17/96. The CCB contained trace amounts (below EQL) of toluene and tetradecane. The CCB was otherwise clean. Both samples contained minor amounts of 1-chloro, 1,1-difluoroethane. This analyte was also present in the field and trip blanks as discussed previously.

**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 BX-110 on 4/30/96

Target Analytes <sup>(a)</sup>	CAS	MW	Ret Time	S6046-A11.969 <sup>(c)</sup>		S6046-A12.970 <sup>(c)(d)</sup>		Mean Values (mg/m <sup>3</sup> ) (ppbv)
				(mg/m <sup>3</sup> )	Flag	(mg/m <sup>3</sup> )	Flag	
Methanol	67-56-1	32	10.1	0.434	303 Y	0.409	286 Y	0.421 294
Ethanol	64-17-5	46.1	12.6	0.796	387 Y	0.316	154 Y	0.556 270
Acetonitrile	75-05-8	41.1	13.1	0.021	11 J	0.022	12 J	0.021 12
Acetone	67-64-1	58.1	13.7	0.354	136	0.321	124	0.337 130
Trichlorofluoromethane	75-69-4	137	14.2	0.017	2.8 J	0.032	5.3 J	0.025 4
Methylene Chloride	75-09-2	84.9	15.8	0.022	5.7 J	0.042	11 J	0.032 8
Propanol	71-23-8	60.1	17.1	0.026	9.6 J	0.035	13 J	0.030 11
2-Butanone	78-93-3	72.1	18.7	0.013	4.2 J	0.017	5.2 J	0.015 5
Butanenitrile	109-74-0	69.1	21.9	0.003	0.94 J	0.003	1.0 J	0.003 1
Benzene	71-43-2	78.1	22.8	0.002	0.46 J	0.001	0.40 J	0.002 0
1-Butanol	71-36-3	74	22.4	0.066	20 J	0.096	29	0.081 25
Pyridine	110-86-1	79.1	26.6	0.037	10 J	0.033	9.3 J	0.035 10
Toluene	108-88-3	92.1	28.5	0.006	1.5 J	0.009	2.1 J	0.007 2
Undecane	1120-21-4	156	44.5	0.017	2.5 J	0.025	3.5 J	0.021 3
Dodecane	112-40-3	170	48.5	0.004	0.52 J	0.026	3.4 U	e
Tridecane	629-50-5	184	52.3	0.032	3.9 J	0.035	4.2 J	0.033 4
Tetradecane	629-59-4	198	55.8	0.067	7.5 J	0.132	15	0.099 11

**Tentatively Identified Compounds<sup>(b)</sup>**

Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.204	46 N	0.132	30 N	0.168 38
Acetaldehyde	75-07-0	44	9.5	0.019	9.5 N	0.063	32 N	0.041 21
Acetic acid	64-19-7	60	18.2	0.032	12 N	0.043	16 N	0.038 14

**Data Quality Flags**

J Target compound detected above the IDL but below the EQL.

N denotes tentatively identified compound

U Target compound not detected at or above the IDL.

Y Initial calibration and CCV was performed; however, the analyte was not part of the current operating procedure.

**Footnotes**

(a) Detected 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 E.3.

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

nd Not Detected

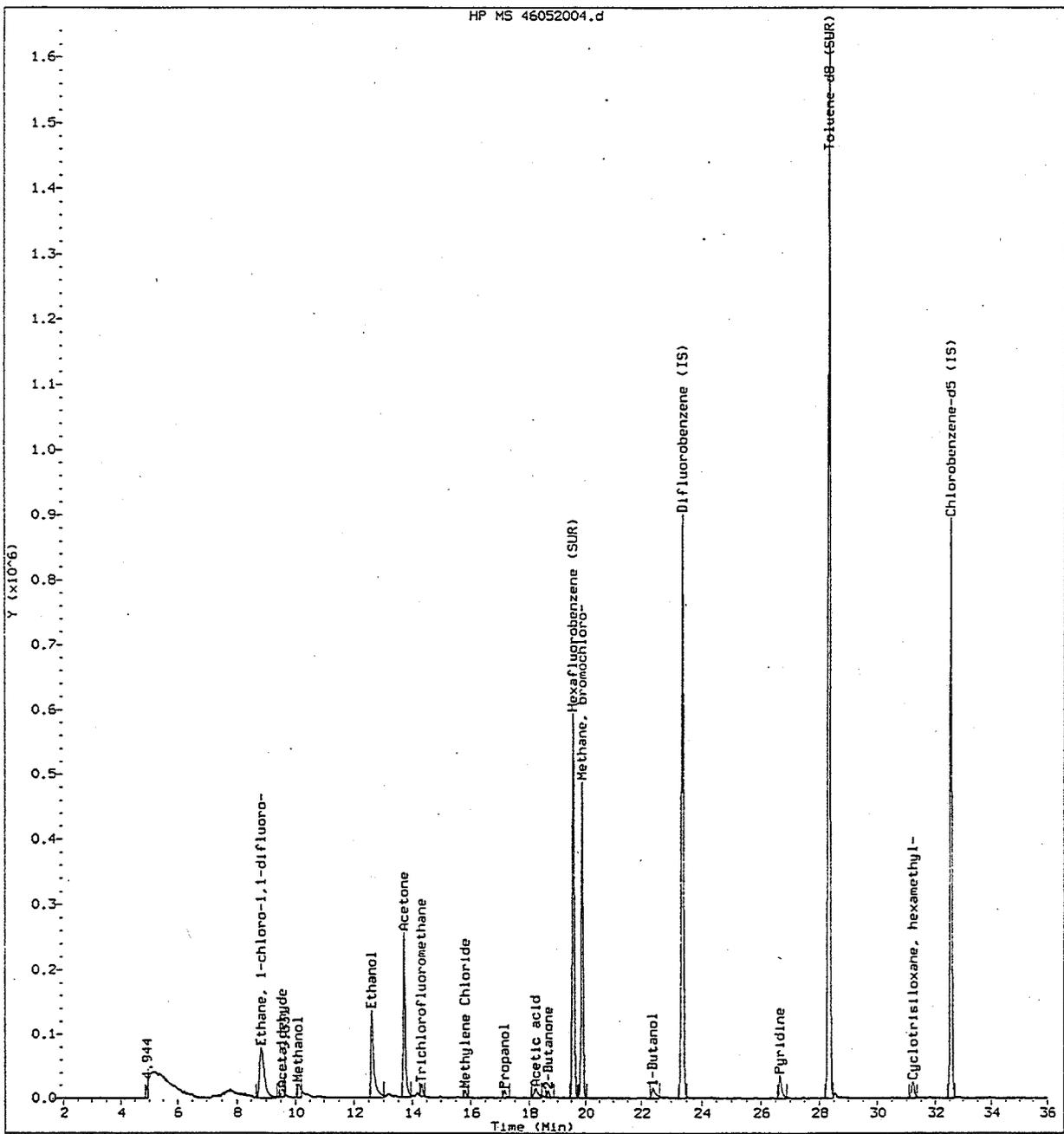
**Table E.3.** Positively Identified and Quantitated Target Analytes<sup>(a)</sup> and Tentatively Identified Compounds and Estimated Concentrations<sup>(b)</sup> of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank BX-110 on 4/30/96

Target Analytes <sup>(a)</sup>	CAS	MW	Ret Time	S6046-A12.970 <sup>(c)</sup>		S6046-A12.970 <sup>(c)</sup>		Relative Percent Difference <sup>(d)</sup>
				(mg/m <sup>3</sup> )	(ppbv)	(mg/m <sup>3</sup> )	(ppbv)	
Methanol	67-56-1	32.04	10.1	0.409	286	0.645	451	45
Ethanol	64-17-5	46.07	12.6	0.316	154	0.472	230	40
Acetonitrile	75-05-8	41.05	13.1	0.022	12	0.029	16	29
Acetone	67-64-1	58.08	13.7	0.321	124	0.324	125	1
Trichlorofluoromethane	75-69-4	137.37	14.2	0.032	5.3	0.035	5.7	7
Methylene Chloride	75-09-2	84.93	15.8	0.042	11	0.047	12.3	10
Propanol	71-23-8	60.1	17.1	0.035	13	0.033	12.3	4
2-Butanone	78-93-3	72.11	18.7	0.017	5.2	0.016	5.0	4
Butanenitrile	109-74-0	69.11	21.9	0.003	1.0	0.003	1.0	3
Benzene	71-43-2	78.11	22.8	0.001	0.40	0.008	2.3	140
1-Butanol	71-36-3	74	22.4	0.096	29	0.085	26	13
Pyridine	110-86-1	79.1	26.6	0.033	9.3	0.031	8.9	5
Toluene	108-88-3	92.14	28.5	0.009	2.1	0.009	2.3	9
Undecane	1120-21-4	156	44.5	0.025	3.5	0.021	3.0	15
Tridecane	629-50-5	184	52.3	0.035	4.2	0.032	3.9	6
Tetradecane	629-59-4	198	55.8	0.132	15	0.129	15	2

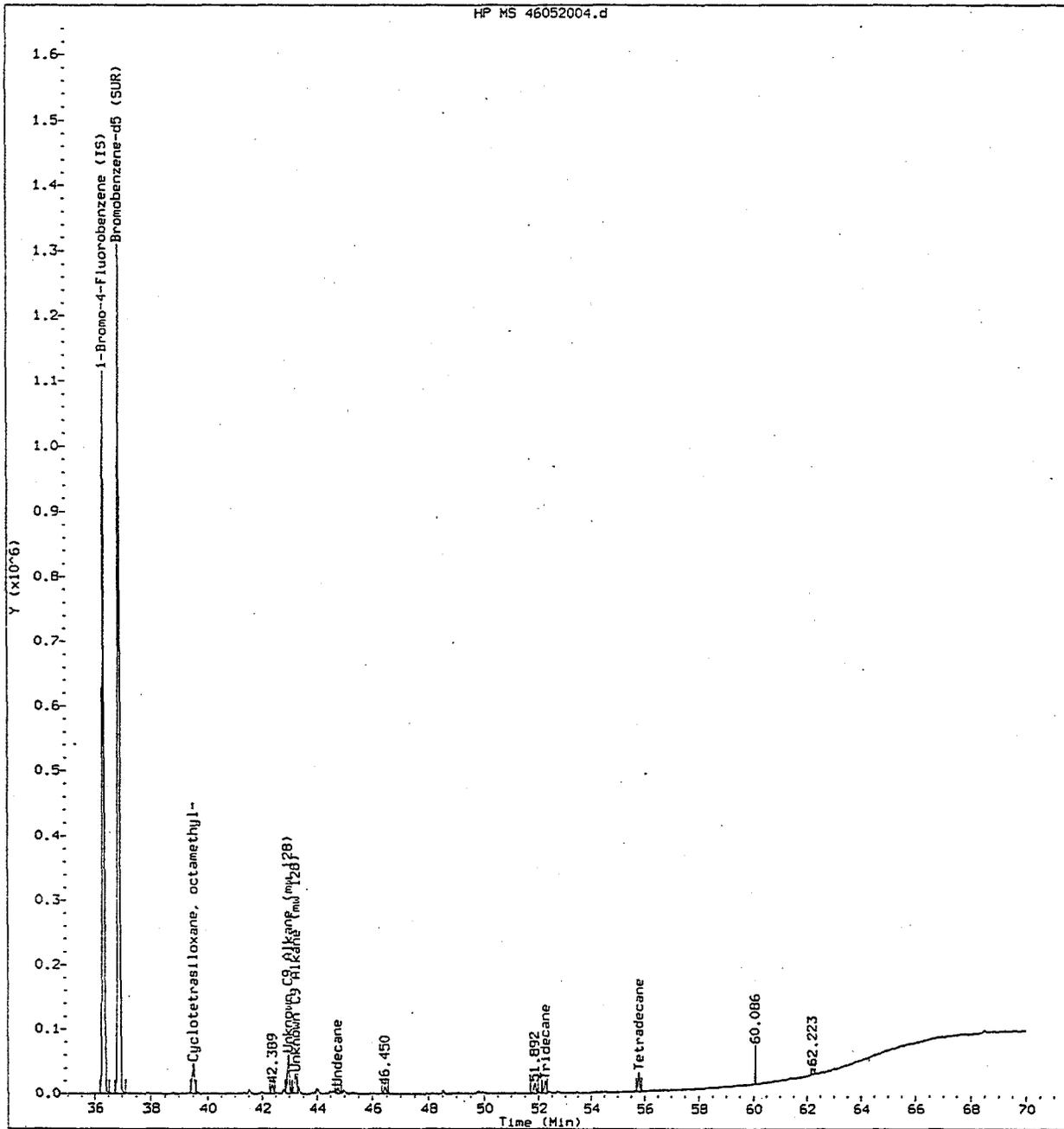
Tentatively Identified Compounds <sup>(b)</sup>	CAS	MW	Ret Time	(mg/m <sup>3</sup> )	(ppbv)	Flag	(mg/m <sup>3</sup> )	(ppbv)	Flag	Relative Percent Difference <sup>(d)</sup>
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.132	30	N	0.113	25	N	15
Acetaldehyde	75-07-0	44	9.5	0.063	32	N	0.025	13	N	86
Acetic acid	64-19-7	60	18.2	0.043	16	N	nd	nd	nd	

**Data Quality Flags**  
 J Target compound detected above the IDL but below the EQL.  
 N denotes tentatively identified compound  
 U Target compound not detected at or above the IDL.  
 Y Initial calibration and CCV was performed; however, the analyte was not part of the current operating procedure.

**Footnotes**  
 (a) Detected target analytes.  
 (b) Semi-quantitative estimate calculated using concentration of closest eluting IS.  
 (c) WHC sample identification number.  
 (d) Relative percent difference based on mg/m<sup>3</sup> values  
 nd Not Detected



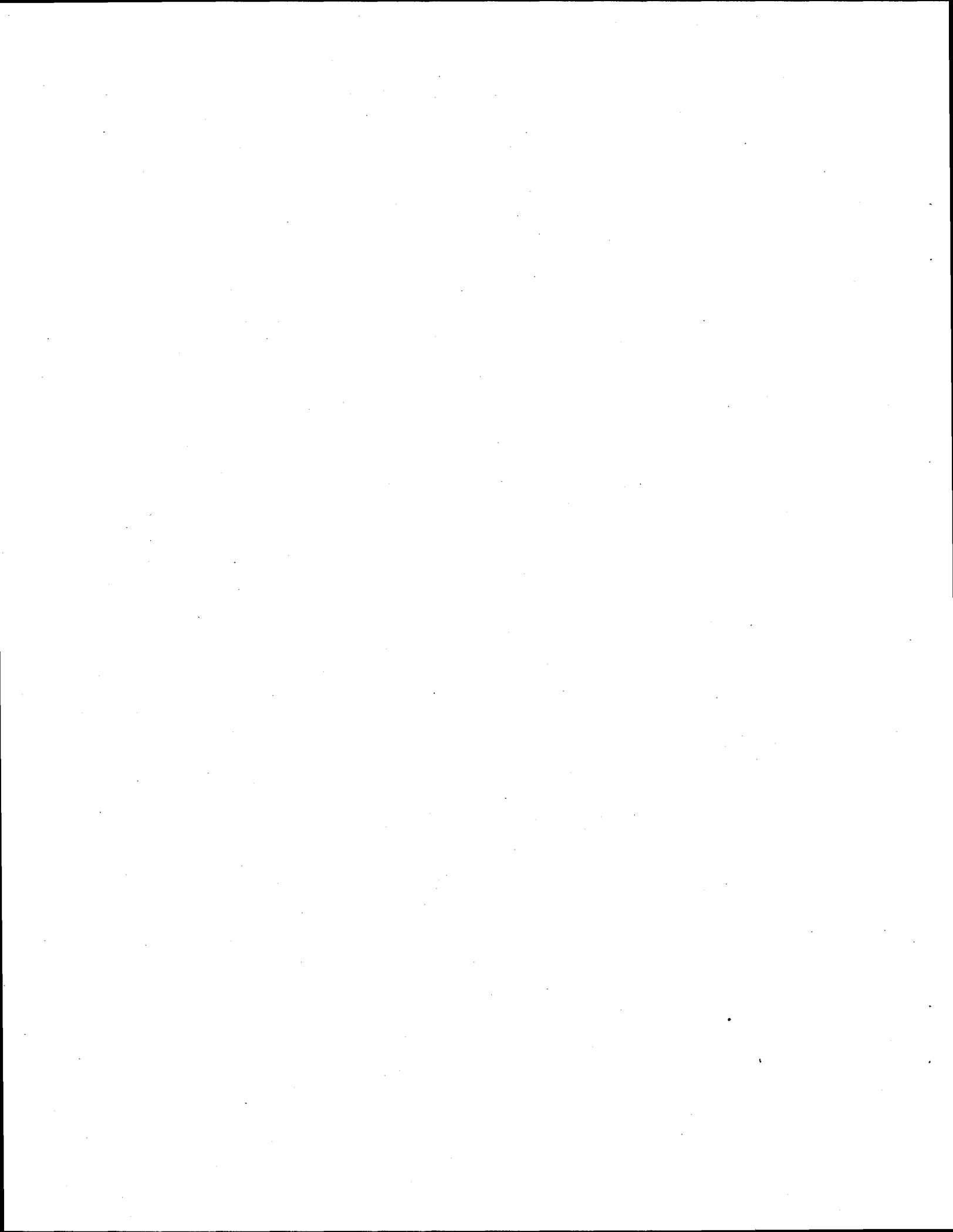
**Figure E.1a** Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank BX-110 Triple Sorbent Trap Sample S6046-A11-969 Collected on 4/30/96



**Figure E.1b** Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank BX-110 Triple Sorbent Trap Sample S6046-A11-969 Collected on 4/30/96

## **Appendix F**

### **Tank Vapor Characterization: Chain of Custody Sample Control Forms**



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

Company Contact R. D. Mahon - WHC Telephone (509) 373-7437  
Page 85-9656 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm Collection date 64 - 30 - 96  
241-BX-110 Tank Vapor Sample SAF S6046 Preparation date 04 - 22 - 96  
VSS

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

Bill of Lading/Airbill No. N/A Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to PNNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6046 - A07 . S67' Collect NH<sub>3</sub>/NO<sub>x</sub>/H<sub>2</sub>O Sorbent Trap  
S6046 - A08 . S68' Collect NH<sub>3</sub>/NO<sub>x</sub>/H<sub>2</sub>O Sorbent Trap  
S6046 - A09 . S69' Collect NH<sub>3</sub>/NO<sub>x</sub>/H<sub>2</sub>O Sorbent Trap  
S6046 - A10 . S70' Collect NH<sub>3</sub>/NO<sub>x</sub>/H<sub>2</sub>O Sorbent Trap

S6046 - A15 . S71' Open, close and store NH<sub>3</sub>/NO<sub>x</sub>/H<sub>2</sub>O field blank #1  
S6046 - A16 . S72' Open, close and store NH<sub>3</sub>/NO<sub>x</sub>/H<sub>2</sub>O field blank #2

[ ] Field Transfer of Custody		[ X ] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
G W Dennis / G.W. Dennis	04-22-96	1330	J.A. Edwards / J.A. Edwards	04-22-96	1330
J.A. Edwards / J.A. Edwards	04-29-96	1510	C.S. McClister / C.S. McClister	04-29-96	1510
C.S. McClister / C.S. McClister	04-29-96	1645	R.D. Mahon / R.D. Mahon	04-29-96	1645
R.D. Mahon / R.D. Mahon	05-15-96	1312	G.S. Caputo / G.S. Caputo	05-15-96	1312
G.S. Caputo / G.S. Caputo	5-15-96	1410	J.A. Edwards / J.A. Edwards	5-15-96	1410
J.A. Edwards / J.A. Edwards	5-17-96	0920	G.W. Dennis / G.W. Dennis	5-17-96	0920
G.W. Dennis / G.W. Dennis	5-20-96	1500	D.O. Slate / D.O. Slate	5-20-96	1500

Final Sample Disposition

Comments:

PNNL (only) Checklist	Pick-up / Delivery	Comments:
Media labeled and checked?	Y/N	
Letter of instruction?	Y/N	
Media in good condition?	Y/N / Y/N	
COC info/signatures complete?	Y/N / Y/N	
Rad release stickers on samples?	/ Y/N	
Activity report from 222S?	/ Y/N	
RSR/copy? (a ≤100/B ≤400 pCi/g)	/ Y/N	
COC copy for LRB, RIDS filed?	/ Y/N	
POC <u>[Signature]</u>	POC <u>[Signature]</u>	

(Revised 11/30/95 PNNL)

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

Company Contact R. D. Mahon - WHC Telephone (509) 373-2891  
Page 85-9656 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm Collection date 04 - 30 - 96  
241-BX-110 Tank Vapor Sample SAF S6046 Preparation date 04 - 29 - 96  
(VSS Truck)

Ice Chest No. Field Logbook No. WHC- N-697-10

Bill of Lading/Airbill No. N/A Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to PNNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6046 - A01 . 115 Collect Ambient Air Sample SUMMA #1 Upwind of Tank  
S6046 - A02 . 121 Collect Ambient Air Sample SUMMA #2 Through VSS

S6046 - A04 . 155 Collect SUMMA #3  
S6046 - A05 . 213 Collect SUMMA #4  
S6046 - A06 . 255 Collect SUMMA #5

[ ] Field Transfer of Custody		[ X ] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
J A Edwards <i>J A Edwards</i>	04-29-96	1510	C S McClellan <i>CSnell</i>	04-29-96	1510
<i>CS McClellan</i> C. S. McClellan	04-29-96	1645	<i>R D Mahon</i> R. D. Mahon	04-29-96	1645
<i>R D Mahon</i> R. D. Mahon	<del>05-15-96</del>	1312	<i>GS CARPIO</i> G. S. Carpio	05-15-96	1312
<i>GS CARPIO</i> G. S. Carpio	5-15-96	1425	<i>J A Edwards</i> J. A. Edwards	5-15-96	1425

Final Sample Disposition

Comments:

PNNL (only) Checklist	Pick-up / Delivery	Comments:
Media labeled and checked?	(Y) N	
Letter of instruction?	(Y) N	
Media in good condition?	(Y) N	
COC info/signatures complete?	(Y) N	
Rad release stickers on samples?	(Y) N	
Activity report from 222S?	(Y) N	
RSR/copy? (a ≤100/B ≤400 pCi/g)	(Y) N	
COC copy for LRB, RIDS filed?	(Y) N	
	POC (R)	POC (F)

(Revised 11/30/95 PNNL)

Custody Form Initiator J. A. Edwards - PNL  
 Company Contact R. D. Mahon - WHC  
 Project Designation/Sampling Locations 200 West Tank Farm  
 241-BX-110 Tank Vapor Sample SAF S6046  
 (VSS Truck)  
 Ice Chest No.  
 Erco Hi/Lo thermometer No. PNL-T-004  
 Bill of Lading/Airbill No. N/A  
 Method of Shipment Government Truck  
 Shipped to WHC-  
 Possible Sample Hazards/Remarks Unknown at time of sampling

Telephone (509) 373-0141  
 Page 85-3009 / P8-08 / FAX 376-0418  
 Telephone (509) 373-7437  
 Page 85-9656 / S3-27 / FAX 373-7076  
 Collection date 04 - 20 - 96  
 Preparation date 04 - 28 - 96  
 Field Logbook No. WHC- N 64710

Offsite Property No. N/A

**Sample Identification**

S6046 - A11 . 969 PNL Triple Sorbent Trap (TST) Sample # 1  
 S6046 - A12 . 970 PNL TST Sample # 2  
 S6046 - A13 . 971 PNL TST Sample # 3  
 S6046 - A14 . 972 PNL TST Sample # 4  
 S6046 - A17 . 975 Open, close & store TST Field Blank # 1 In VSS truck  
 S6046 - A18 . 976 Open, close & store TST Field Blank #2 In VSS truck  
 S6046 - A19 . 977 Store TST Trip Blank #1  
 S6046 - A20 . 978 Store TST Trip Blank #2

[ ] Field Transfer of Custody		[ X ] Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
JL Julva	04-29-96	1215	JA Edwards	04-29-96	1215	
JA Edwards	04-29-96	1510	CS Medina	04-29-96	1510	
CS Medina	04-29-96	1643	RDMahon	04-29-96	1643	
RDMahon	05-15-96	1312	CS Caprio	05-15-96	1312	
CS Caprio	5-15-96	1410	JA Edwards	5-15-96	1410	
JA Edwards	5-15-96	1410	JL Julva	5-15-96	1410	

**Final Sample Disposition**

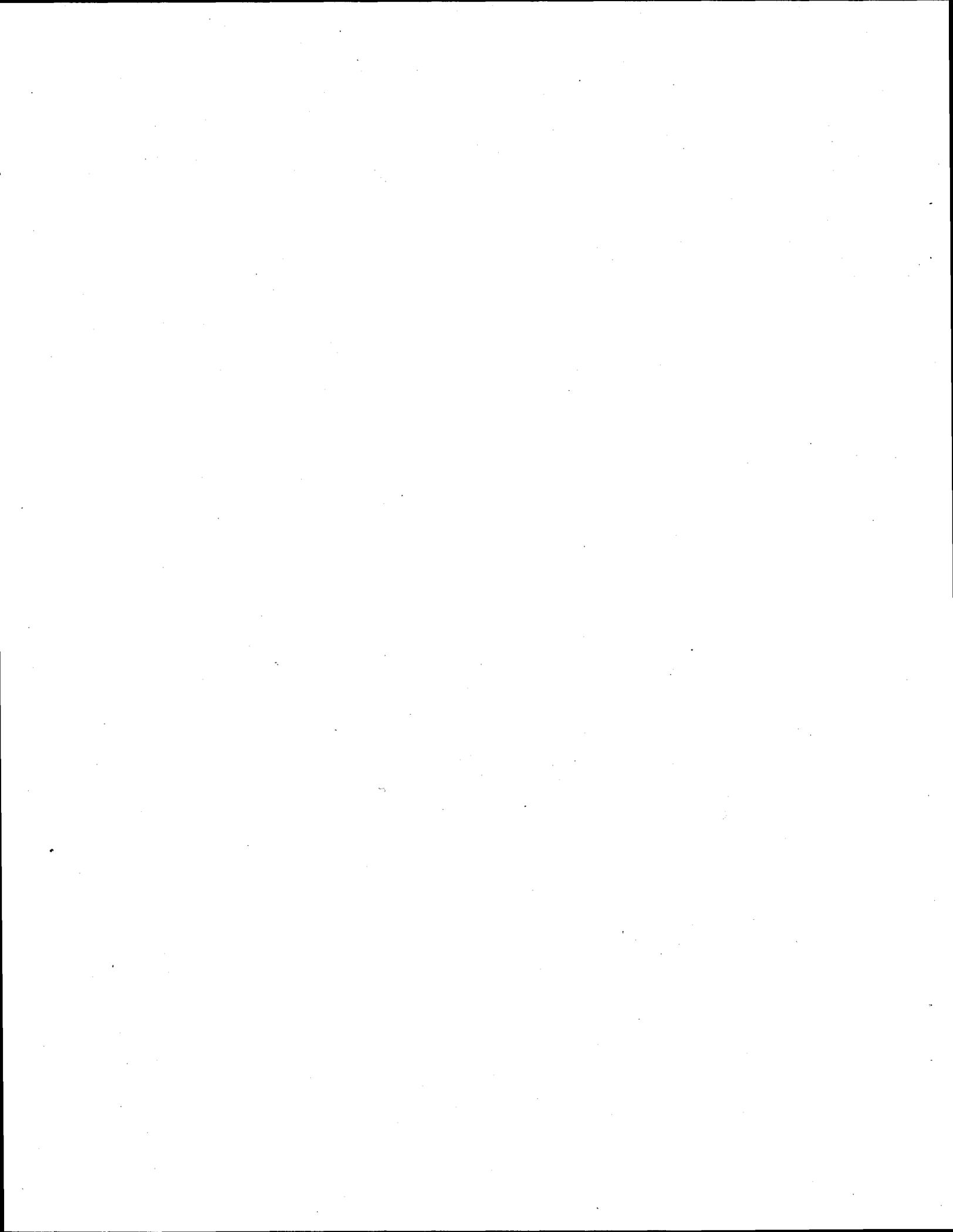
**Comments:**

- 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
- POC  POC

**Comments:**

Cooler Temperature Status  
 Hi -18 °C / Lo -18 °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 +5 °C / Lo -14 °C (at delivery from WHC to PNL) |

(Revised 06/21/95 PNL)



**Distribution List**

**PNNL-11256**

**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
Kris Walters	K6-80 (5 copies)

**Lockheed**

Larry Pennington	S7-21
Luther Buckley	R2-12

**DOE-RL**

Carol Babel	S7-54
Jim Thompson	S7-54

