

# Pacific Northwest National Laboratory

Operated by Battelle for the  
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## TANK VAPOR CHARACTERIZATION PROJECT

### Headspace Vapor Characterization of Hanford Waste Tank 241-T-104: Results from Samples Collected on 02/07/96

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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**

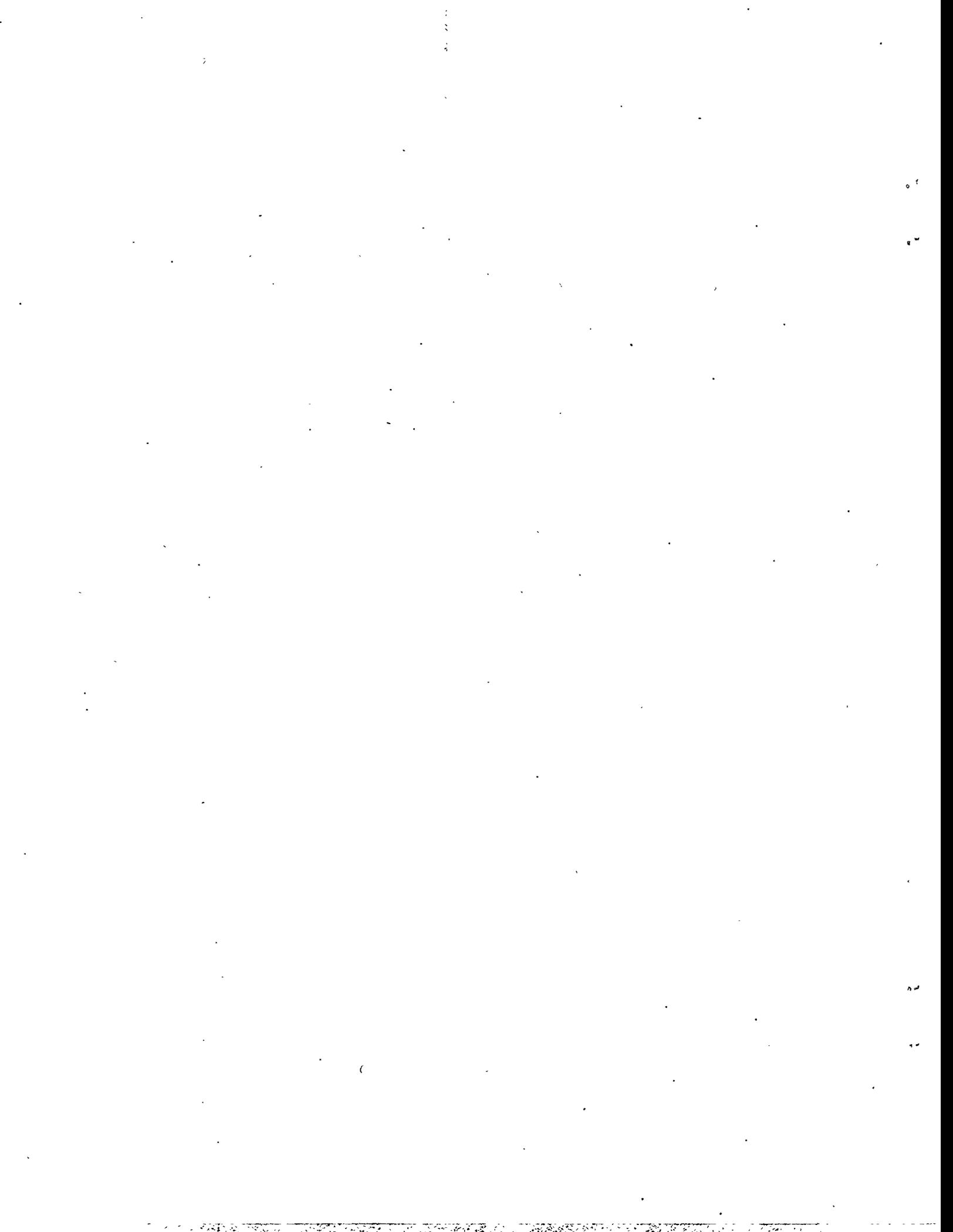
### **Headspace Vapor Characterization of Hanford Waste Tank 241-T-104: Results from Samples Collected on 2/07/96**

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Richland, Washington 99352



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## Summary

This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-T-104 (Tank T-104) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support safety evaluations and tank farm operations. The results include air concentrations of selected inorganic and organic analytes and grouped compounds from samples obtained by Westinghouse Hanford Company (WHC) and provided for analysis to Pacific Northwest National Laboratory (PNNL). Analyses were performed by the Vapor Analytical Laboratory (VAL) at PNNL. Analyte concentrations were based on analytical results and, where appropriate, on sample volumes provided by WHC. A summary of the inorganic analytes, permanent gases, and total non-methane hydrocarbons is listed in Table S.1. Detailed descriptions of the analytical results appear in the appendices.

**Table S.1.** Summary Results of Samples to Characterize the Headspace of Tank T-104 on 2/07/96

<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>	105 ± 3	ppmv
		NO <sub>2</sub>	0.3 ± 0.1	ppmv
		NO	0.3 ± 0.2	ppmv
		H <sub>2</sub> O	12.0 ± 0.5	mg/L
Permanent Gases	SUMMA™ Canister	CO <sub>2</sub>	241	ppmv
		CO	3 U	ppmv
		CH <sub>4</sub>	4 U	ppmv
		H <sub>2</sub>	12 J	ppmv
		N <sub>2</sub> O	8 J	ppmv
Total Non-Methane Hydrocarbons (TO-12)	SUMMA™ Canister	Hydrocarbons	1.93	mg/m <sup>3</sup>

(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.

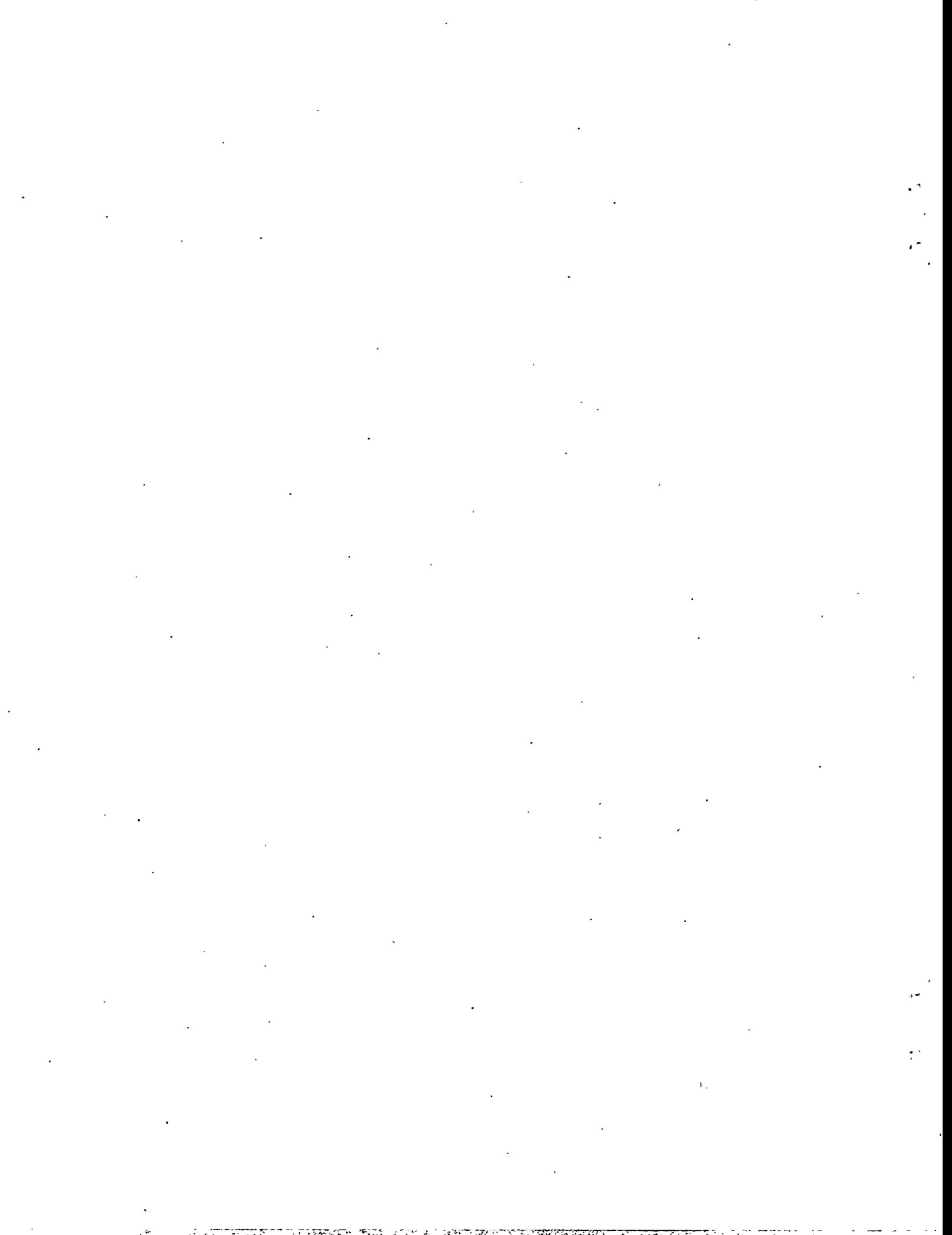
### Data Qualifier Flags

J = Target compound detected above the Instrument Detection Limit (IDL) but quantitated amount below Estimated Quantitation Limit (EQL).

U = Target compound not detected at or above the IDL.

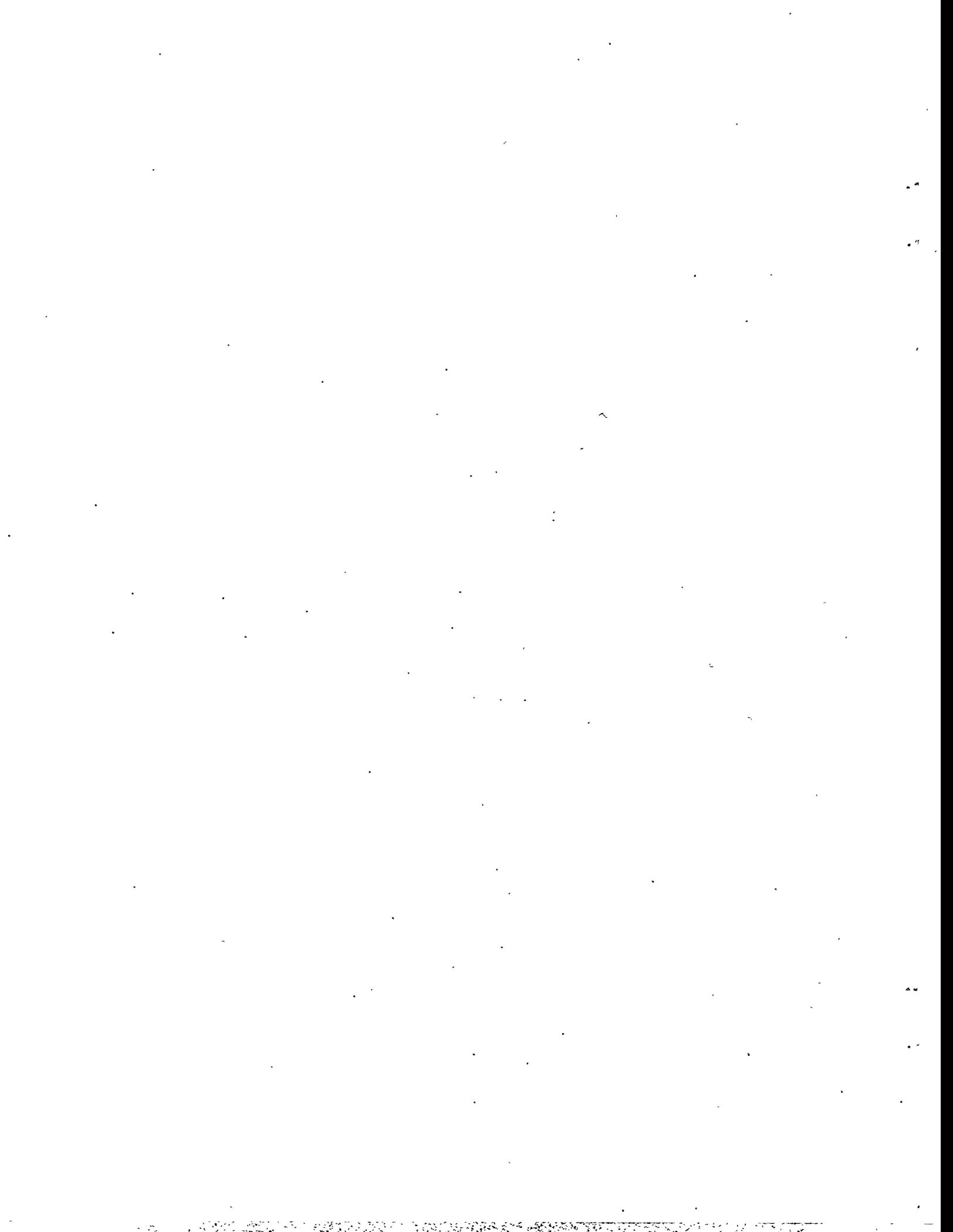
## Acknowledgments

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



## Glossary

CAS	Chemical Abstracts Service
CCV	continuing calibration verification
COC	chain-of-custody
C <sub>v</sub>	concentration by volume
DIW	deionized water
EPA	U.S. Environmental Protection Agency
EQL	estimated quantitation limit
GC/FID	gas chromatography/flame ionization detector
GC/TCD	gas chromatography/thermal conductivity detection
IC	ion chromatography
IDL	instrument detection limit
IL	impact level
IS	internal standard
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
TNMHC	total non-methane hydrocarbons
UHP	ultra high purity
VAL	Vapor Analytical Laboratory
VSS	vapor sampling system
WHC	Westinghouse Hanford Company



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## 1.0 Introduction

This report describes the results of vapor samples taken from the headspace of waste storage tank 241-T-104 (Tank T-104) 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 1996), and the sample job was designated S6012. Samples were collected by WHC on February 7, 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 11 sorbent trains for selected inorganic analytes (eight sample trains and three field blanks) and five SUMMA™ canisters for permanent gases and total non-methane hydrocarbons (three sample and two ambient canisters). The samples and controls were provided to WHC on January 30, 1996. Exposed samples and controls were returned to PNNL on February 8, 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 canister samples were analyzed for

- *permanent gases* using gas chromatography/thermal conductivity detection (GC/TCD)
- *total non-methane hydrocarbons* using cryogenic preconcentration followed by gas chromatography/flame ionization detection (GC/FID).

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

(b) PNL-TVP-07, Rev. 0, October 1994, *Sample Shipping and Receiving Procedure for PNL Waste Tank Samples*, PNL Technical Procedure, Tank Vapor Project, Pacific Northwest Laboratory, Richland, Washington.

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, and C. Appendix D contains the completed COC forms.

## 2.0 Analytical Results

Samples obtained by WHC from the headspace of Tank T-104 on February 7, 1996, (Sample Job S6012) 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  $105 \pm 3$  ppmv ( $\text{NH}_3$ ),  $0.3 \pm 0.1$  ppmv ( $\text{NO}_2$ ),  $0.3 \pm 0.2$  ppmv ( $\text{NO}$ ), and  $12.0 \pm 0.5$  mg/L (primarily  $\text{H}_2\text{O}$ ). The vapor concentration results were based on six samples for each compound (eight samples for mass concentration). The  $\text{NO}_2$  and  $\text{NO}$  samples included four samples trailing (downstream of)  $\text{NH}_3$  sorbent traps and two samples unprotected by  $\text{NH}_3$  sorbent traps. Representative field blanks were also analyzed and used to correct data.

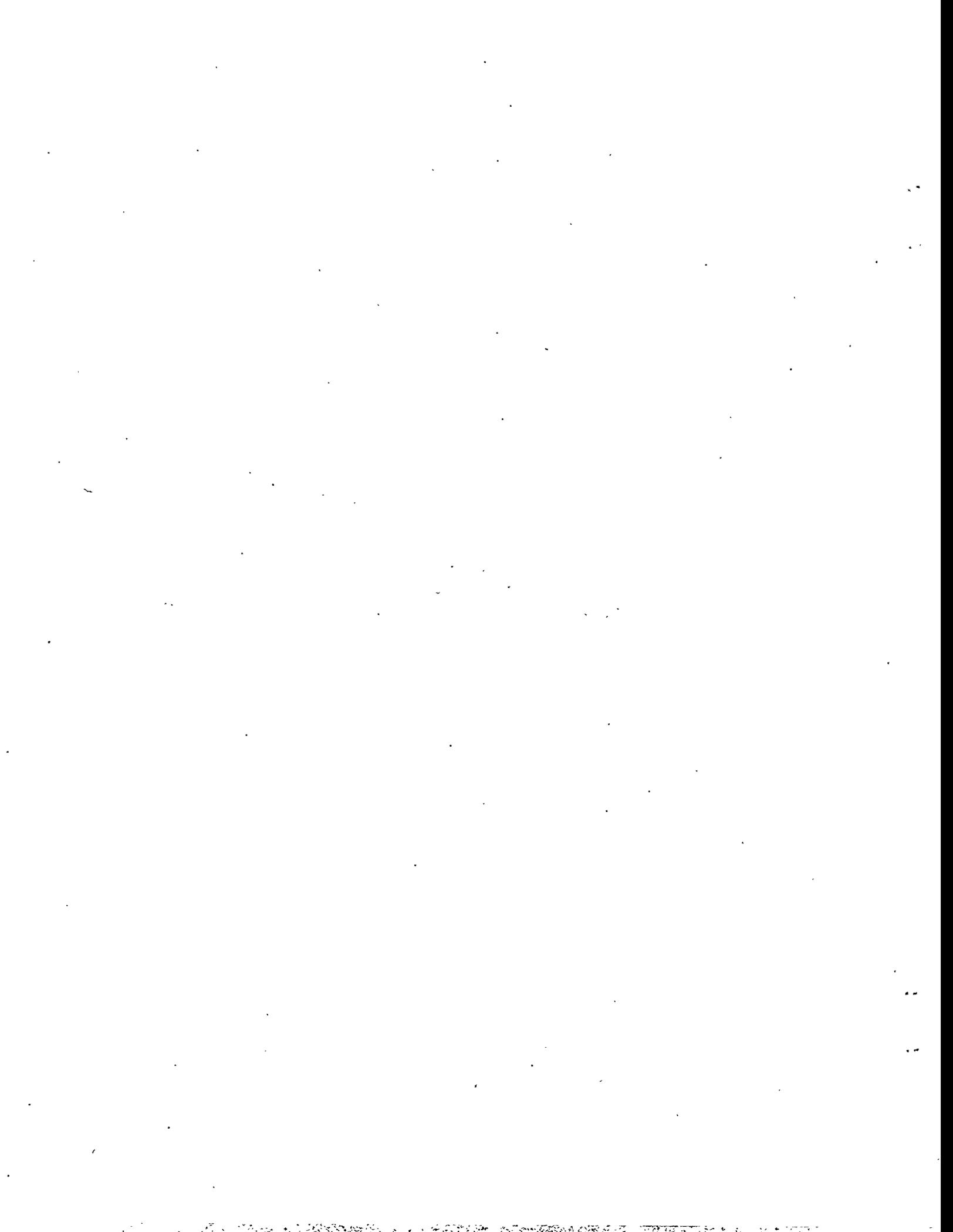
Results provided above are estimated to be accurate to within  $\pm 10\%$  (assuming negligible error in the sample volume measurements) and are within the  $\pm 30\%$  specified by the SAP. Measurement precision, as indicated by the relative standard deviation, was  $< 5\%$  for each of the compounds found to be present at concentrations significantly greater than the analytical method estimated quantitation limit (EQL), and within the 25% specified by the SAP. All samples were analyzed within 20 days after being collected. No deviations from standard procedures were noted. These uncertainties were confirmed by evaluation of spikes and continuing calibration standards ( $\text{NH}_3$ ) and evaluation of the variability of field blanks ( $\text{H}_2\text{O}$ ). Data and additional information on samples, analyses, and results are described in Appendix A. The chain-of-custody form used to control samples, 100035, is included in Appendix D.

### 2.2 Permanent Gases

The complete results of the permanent gas analysis of Tank T-104 can be found in Appendix B of this report. In summary, carbon dioxide at 241 ppmv was the only permanent gas observed above the method EQL in the tank headspace samples, and carbon dioxide in the headspace samples was at a lower concentration than observed in the ambient air.

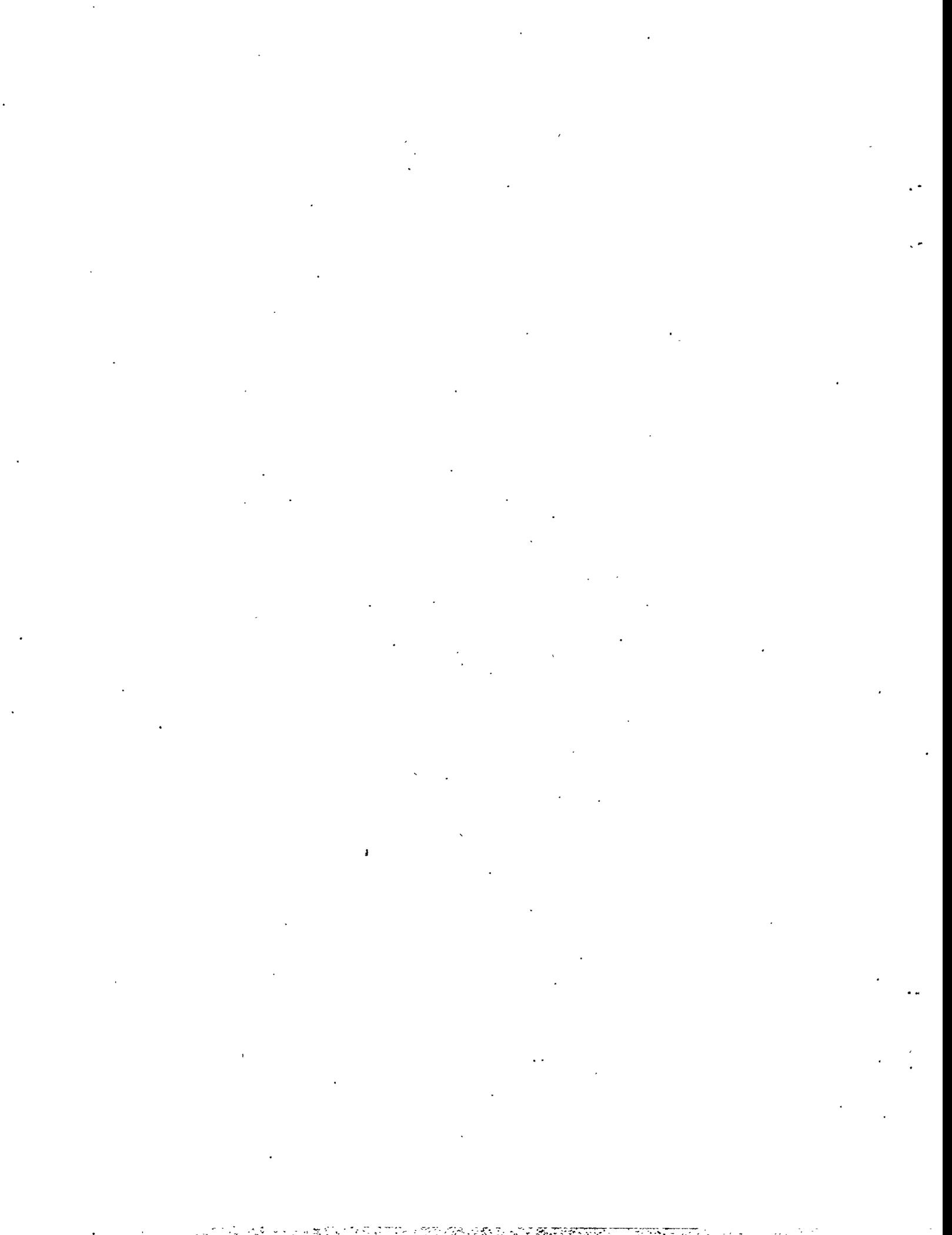
### 2.3 Total Non-Methane Hydrocarbons

The complete results of the TO-12 analysis of Tank T-104 can be found in Appendix C of this report. In summary, the average concentration in the three tank headspace samples was  $1.93 \text{ mg/m}^3$ .



### 3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank T-104 collected on February 7, 1996 (Sample Job S6012). The vapor concentrations were based either on whole-volume samples (SUMMA™ canisters) or on sorbent traps exposed to sample flow. In the case of the canisters, the concentrations were based on analytical results and the tracking of dilution/concentration of sample volumes obtained directly from the canisters. In the case of the sorbent traps, concentrations were based on analytical results and sample volumes reported by WHC. Known sampling and analytical variances from established QA requirements, where significant, were documented in this report, as required by the SAP (Homi 1996).



## 4.0 Reference and Further Reading

### Reference

Homi, C.S. 1996. *Vapor Sampling and Analysis Plan*. WHC-SD-WM-TP-335, Rev. 1D, Westinghouse Hanford Company, Richland, Washington.

### Further Reading

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

Pacific Northwest Laboratory. *Quality Assurance Manual, Part 3: Procedures for Quality Assurance Program*. PNL-MA-70, Part 3, Pacific Northwest Laboratory, Richland, Washington.

Pacific Northwest National Laboratory. *Quality Assurance Plan for Activities Conducted by the Pacific Northwest National Laboratory Vapor Analytical Laboratory (VAL) and the Pacific Northwest National Laboratory Tank Vapor Characterization Project*. ETD-002, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

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

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

## **Appendix A**

### **Tank Vapor Characterization:**

### **Inorganic Analytes**

## Appendix A

### Tank Vapor Characterization: Inorganic Analytes

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to Westinghouse Hanford Company (WHC) for sampling the tank headspace using the Vapor Sampling System (VSS). Blanks, spiked blanks (when requested), and exposed samples were returned to Pacific Northwest National Laboratory (PNNL) for analysis. Analyses were performed to provide information on the tank headspace concentration of the following analytes: ammonia ( $\text{NH}_3$ ), nitrogen dioxide ( $\text{NO}_2$ ), nitric oxide (NO), and water ( $\text{H}_2\text{O}$ ). Procedures were similar to those developed previously during sample jobs performed with the VSS connected to the headspace of Tank C-103 (Ligotke et al. 1994). During those sample jobs, control samples provided validation that the 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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(a) Pacific Northwest Laboratory. 10/94. *Sorbent Trap Preparation for Sampling and Analysis: Waste Tank Inorganic Vapor Samples*, PNL-TVP-09 (Rev. 0), PNL Technical Procedure, 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. All were compiled in PNL-MA-599.

**A.2.1 Ammonia Analysis.** The sorbent material from the  $\text{NH}_3$ -selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-, or primary-, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the  $\text{NH}_3$  sorbent traps were analyzed using the selective ion electrode procedure PNL-ALO-226<sup>(a)</sup>. Briefly, this method includes 1) preparing a 1000- $\mu\text{g}/\text{mL}$  (ppm)  $\text{NH}_3$  stock standard solution from dried reagent-grade  $\text{NH}_4\text{Cl}$  and DIW, 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm  $\text{NH}_3$  working calibration standards by serial dilution of the freshly made stock standard, 3) generating an initial calibration curve from the measured electromotive force signal versus  $\text{NH}_3$  concentration data obtained for the set of working standards, 4) performing a calibration-verification check, using a mid-range dilution of a certified National Institute for Standards and Technology (NIST)-traceable 0.1 M  $\text{NH}_4\text{Cl}$  standard from an independent source, after analyzing every five or six samples, 5) continuing this sequence until all samples of the batch have been measured, including duplicates and spiked samples, and 6) remeasuring the complete set of calibration standards (at the end of the session). 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

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

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

Instrument responses (peak height) observed for samples were compared to those for standards to determine the nitrite concentration of the samples. Because  $\text{NO}_2$  and  $\text{NO}$  converted to  $\text{NO}_2$  were collected on the sorbent as equal quantities of nitrite and nitrate, and the analysis was specific for nitrite, the molar masses of  $\text{NO}_2$  and  $\text{NO}$  were determined by doubling the analytically determined molar mass of nitrite.

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

### A.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNNL documents. The samples were analyzed following PNNL Impact Level II. The PNNL documents include PNL-MA-70 (Part 3), PNL-ALO-212, PNL-ALO-226, and ETD-002. 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>**

<u>Analyte</u>	<u>Formula</u>	<u>Procedure</u>	<u>EQL<sup>(b)</sup> (<math>\mu</math>g)</u>	<u>EQL<sup>(b)</sup> (ppmv)</u>	<u>Notification Level<sup>(c)</sup> (ppmv)</u>
Ammonia	NH <sub>3</sub>	PNL-ALO-226	1.0	0.5	≥ 150
Nitrogen Dioxide	NO <sub>2</sub>	PNL-ALO-212	0.3	0.1	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.3	0.1	≥ 50
Mass (water) <sup>(d)</sup>	n/a	PNL-TVP-09	0.6 mg	0.2 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 T-104 on February 7, 1996 using the VSS. The sample job designation number was S6012. Samples were prepared, submitted to WHC for the sample job, and then returned to PNL and analyzed to provide information on the concentrations of NH<sub>3</sub>, NO<sub>2</sub>, NO, and mass (primarily H<sub>2</sub>O). Samples were controlled using chain-of-custody 100035 (Appendix D). The inorganic samples were received from WHC on February 8, 1996; the sample volume information was also received on February 8. Analyses were completed on February 13, (gravimetric, 6 days elapsed), February 23 (ammonia, 16 days elapsed), and February 27 (nitrite, 20 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 were nearly indistinguishable from those of blanks, indicating very

low vapor concentrations of the analyte, the concentration results (Table A.3) are listed as "less-than-or-equal-to" a probable maximum value determined by subtracting the average of the blanks less one standard deviation from the average of the samples plus one standard deviation. Results of control samples, such as trip blanks, field blanks, and spiked blanks, are discussed in this section. Spiked blanks, when used, were transported to the field but not opened. Spiked samples, when used, were opened in the field and used to collect tank vapors. Sample results were not corrected for the percentage recoveries of spiked blanks.

**A.4.1 Ammonia Results.** The concentration of  $\text{NH}_3$  was  $105 \pm 3$  ppmv, based on all six samples. The blank-corrected  $\text{NH}_3$  quantities in the sorbent traps ranged from 13.6 to 14.8  $\mu\text{mol}$  in front sections; blank-corrected  $\text{NH}_3$  was not found ( $\leq 0.01 \mu\text{mol}$ ) in back sorbent sections. Blank corrections, 0.06  $\mu\text{mol}$  in front and 0.03  $\mu\text{mol}$  in back sections, were about 0.4% of collected quantities. The analysis of one sample was duplicated and yielded repeatability of  $\pm 2\%$ . One blank sorbent trap was spiked with roughly the quantity of  $\text{NH}_3$  in the samples and yielded a percentage recovery of 105%. One sample leachate was spiked after initial analysis with roughly the quantity of  $\text{NH}_3$  in the sample and yielded a percentage recovery of 110%. The initial and continuing calibration verification standards, using NIST-traceable material, yielded percentage recoveries of 101% (ICV) and 102 and 105% (CCV) during the analytical session. A five-point calibration was performed over an  $\text{NH}_3$  range of 0.1 to 1000  $\mu\text{g/mL}$ .

**A.4.2 Nitrogen Oxides Results.** It is not known whether the presence of an upstream  $\text{NH}_3$  trap typically affects downstream measurements of  $\text{NO}_2$  and  $\text{NO}$ . Consequently, measurements of  $\text{NO}_2$  and  $\text{NO}$  were made using four "protected" four-segment  $\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$  and two "unprotected" four-segment  $\text{NO}_x/\text{H}_2\text{O}$  sorbent-trap trains. (The  $\text{NO}_x$  trains consisted of three segments:  $\text{NO}_2$  trap, oxidizer,  $\text{NO}_2$  trap.) No clear conclusion could be drawn from the small levels of  $\text{NO}_2$  and  $\text{NO}$  detected in the samples. Because this result varies from tank to tank, measurements using the two types of sorbent trap trains are planned to be continued during subsequent sample jobs for which  $\text{NO}_x$  measurements are required. No further evaluation is required of the results from this sample job.

The concentrations of  $\text{NO}_2$  and  $\text{NO}$  were  $0.3 \pm 0.1$  and  $0.3 \pm 0.2$  ppmv, respectively based on five of the samples. Blank-corrected  $\text{NO}_2^-$  quantities in the sorbent traps averaged 0.018  $\mu\text{mol}$  ( $\text{NO}_2$  samples) and 0.021  $\mu\text{mol}$  ( $\text{NO}$  samples). Nitrite blank levels used to correct data were  $0.0044 \pm 0.0003 \mu\text{mol}$  in front (three of six blanks analyzed) and  $0.0028 \pm 0.0003 \mu\text{mol}$  in back (2 of 6 blanks analyzed) sorbent sections. The analyses of three samples were duplicated and yielded repeatabilities of  $\pm 0.4\%$ ,  $\pm 1.4\%$ , and  $4.9\%$ . Four sample leachates were spiked with  $\text{NO}_2^-$  and yielded percentage recoveries of 93%, 88%, 103%, and 96%. Several of the back sorbent sections in the  $\text{NO}_x$  sample trains were found to have abnormally high concentrations of  $\text{NO}_2^-$ . Contamination during sample handling in the laboratory or in the field is suspected but has not been definitively proven. A four-point calibration was performed over a concentration range of 0.1 to 0.5  $\mu\text{g NO}_2^-$  per mL in the desorbing matrix. Although spiked field 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 (Claus et al. 1994; Ligothke et al. 1994). A spiked preparation blank showed 88% recovery of a 0.25  $\mu\text{g/mL}$  spike.

**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  $\mu\text{g/L}$ , are typically two or three orders of magnitude less than the  $\text{mg/L}$  mass concentrations of the water vapor found in even relatively dry tanks. The water vapor mass

concentration collected in the four- and five-trap sorbent trains was  $12.0 \pm 0.5$  mg/L, based on dry air sample volumes ( $0^{\circ}\text{C}$  and 760 torr). The result was determined from an average mass gain of 36.5 mg from all eight ( $\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$  and  $\text{NO}_x/\text{H}_2\text{O}$ ) sample trains. The blank correction applied to the results was - 0.4 mg per train, based on a mass gain of  $0.4 \pm 0.1$  mg per three 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 of water was  $103 \pm 2\%$  during a previous sample job (Clauss et al. 1994).

Corrected for a measured tank headspace temperature of  $14.3^{\circ}\text{C}$  and pressure of 740.5 torr, the actual water vapor mass concentration from the gravimetric results was  $11.0 \pm 0.4$  mg/L. Also based on analytical results, the partial pressure of water vapor was  $10.9 \pm 0.5$  torr, the relative humidity was  $89 \pm 3\%$ , and the dew point was  $12.5 \pm 0.5^{\circ}\text{C}$ .

**Table A.2** List of PNNL Inorganic Samples, Controls, and Gravimetric Results Obtained from a Heated Tube Inserted into the Headspace of Tank T-104 on 2/7/96

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)
<b>Samples:</b>						
S6012-A04-96S	NH3/NOx/H2O	1	200.0	15.0	3.00	0.0351
S6012-A05-97S	NH3/NOx/H2O	2	200.0	15.0	3.00	0.0353
S6012-A06-98S	NOx/H2O	3	200.0	15.0	3.00	0.0383
S6012-A07-99S	NH3/H2O/H2O	4	200.0	15.0	3.00	0.0381
S6012-A13-S01	NH3/NOx/H2O	1	200.0	15.0	3.00	0.0353
S6012-A14-S02	NH3/NOx/H2O	2	200.0	15.0	3.00	0.0351
S6012-A15-S03	NOx/H2O	3	200.0	15.0	3.00	0.0374
S6012-A16-S04	NH3/H2O/H2O	4	200.0	15.0	3.00	0.0376
<b>Controls:</b>						
S6012-A31-S05	NH3/NOx/H2O Field Blank	n/a <sup>(b)</sup>	n/a	n/a	n/a	0.0004
S6012-A32-S06	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	0.0003
S6012-A33-S07	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	0.0004

(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 T-104 on 2/7/96

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>14.1</u>	<u>3.00</u>	<u>105 <math>\pm</math> 3</u>
S6012-A04-96S	13.7	0.04	13.6	3.00	102
S6012-A05-97S	14.0	NA <sup>(c)</sup>	14.0	3.00	104
S6012-A07-99S	14.5	<0.03	14.4	3.00	108
S6012-A13-S01	13.9	NA	13.8	3.00	103
S6012-A14-S02	14.2	NA	14.1	3.00	105
S6012-A16-S04	14.8	NA	14.8	3.00	110
<u>NO<sub>2</sub> Samples:</u>			<u>0.0180</u>	<u>3.00</u>	<u>0.3 <math>\pm</math> 0.1</u>
S6012-A04-96S	0.0288	0.5559	0.0244	3.00	0.4
S6012-A05-97S	0.0129	0.1207	0.0085	3.00	0.1
S6012-A06-98S <sup>(d)</sup>	0.0204	0.0142	0.0160	3.00	0.2
S6012-A13-S01	0.0264	0.0082	0.0220	3.00	0.3
S6012-A14-S02	0.0235	0.0027	0.0191	3.00	0.3
S6012-A15-S03 <sup>(d)</sup>	0.0048	0.0028	<0.0065	3.00	n/a
<u>NO Samples:</u>			<u>0.0209</u>	<u>3.00</u>	<u>0.3 <math>\pm</math> 0.2</u>
S6012-A04-96S	0.0182	0.4504	0.0138	3.00	0.2
S6012-A05-97S	0.0278	0.3261	0.0234	3.00	0.3
S6012-A06-98S <sup>(d)</sup>	0.0503	0.2821	0.0459	3.00	0.7
S6012-A13-S01	0.1659 x <sup>(c)</sup>	0.0045	0.1615 x	3.00	2.4 x
S6012-A14-S02	0.0183	0.0040	0.0139	3.00	0.2
S6012-A15-S03 <sup>(d)</sup>	0.0121	0.0611	0.0077	3.00	0.1
<u>Gravimetric Samples:</u>			<u>36.1 mg</u>	<u>3.00</u>	<u>12.0 <math>\pm</math> 0.5 mg/L</u>
S6012-A04-96S	n/a <sup>(c)</sup>	n/a	34.7	3.00	11.6
S6012-A05-97S	n/a	n/a	34.9	3.00	11.6
S6012-A06-98S	n/a	n/a	37.9	3.00	12.6
S6012-A07-99S	n/a	n/a	37.7	3.00	12.6
S6012-A13-S01	n/a	n/a	34.9	3.00	11.6
S6012-A14-S02	n/a	n/a	34.7	3.00	11.6
S6012-A15-S03	n/a	n/a	37.0	3.00	12.3
S6012-A16-S04	n/a	n/a	37.2	3.00	12.4

- (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; x = excluded from average.
- (d) NO<sub>x</sub> sorbent traps not preceded by an NH<sub>3</sub> trap. Only selected back sorbent sections were analyzed. Results show back sections of ammonia and nitrite samples routinely contain insignificant quantities of the analytes.

## A.5 References

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

Ligothke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/2/94 - 5/25/94)*. PNL-10172, Pacific Northwest Laboratory, Richland, Washington.

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

## **Appendix B**

### **Tank Vapor Characterization:**

#### **Permanent Gases**

## Appendix B

### Tank Vapor Characterization: Permanent Gases

#### B.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant-free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02<sup>(a)</sup>. The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis. 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 the derived instrument detection limit (IDL) and established EQL 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. 8/94. *Analysis Method for the Determination of Permanent Gases in Hanford Waste Tank Vapor Samples Collected in SUMMA™ Passivated Stainless Steel Canisters*, PNL-TVP-05 (Rev. 1). 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>Instrument Detection Limit (ppmv)</u>	<u>Estimated Quantitation Limit (ppmv)</u>
Carbon Dioxide	CO <sub>2</sub>	PNL-TVP-05	2.4	24
Carbon Monoxide	CO	PNL-TVP-05	3.2	32
Methane	CH <sub>4</sub>	PNL-TVP-05	4.3	43
Hydrogen	H <sub>2</sub>	PNL-TVP-05	3.1	31
Nitrous Oxide	N <sub>2</sub> O	PNL-TVP-05	2.0	20

### **B.3 Quality Assurance/Quality Control**

Standards for the permanent gas analysis were blended from commercially prepared and certified standards for each of the analytes reported in Table B.1. The instrument was calibrated for CO, CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub> over a range of 25 to 2100 parts per million by volume (ppmv) using standards at five different concentrations and He as a carrier gas. A similar procedure was followed for H<sub>2</sub>, except the carrier gas was changed to N<sub>2</sub>. An average response factor from the calculation was used for qualification of compound peak area.

Each analyte was quantitated by comparison of sample analyte peak area to the calibration plot generated for the compound. An IDL study was conducted and performance data are presented in Table B.1. The EQL for the method has also been established as 10 times the IDL. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within  $\pm 25\%$  of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N<sub>2</sub> reagent blank, an ambient-air sample collected  $\sim 10$  m upwind of Tank T-104, 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**

Five SUMMA™ canisters were returned to the laboratory on February 8, 1996, under Westinghouse Hanford Company (WHC) chain-of-custody 100033 (see Appendix D). The samples were analyzed on February 13 and 14, 1996.

Table B.2 lists results of the permanent gas analysis from samples collected from the headspace of Tank T-104, ambient air collected  $\sim 10$  m upwind of the tank, and ambient air collected through the VSS. Carbon dioxide at 241 ppmv was observed above the method EQL in the tank headspace samples. Carbon dioxide in the headspace was at a lower concentration than observed in the ambient air. A duplicate analysis was performed on SUMMA™ canister PNL 041; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

Table B.2 Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank T-104 and for Ambient Air and Ambient Air Through the VSS Collected near Tank T-104 in SUMMA (TM) Canisters on 02/07/96

Permanent Gas Analyte	Ambient Air Upwind		Ambient Air Through VSS		Tank Samples				Average Concentration Tank Samples (ppmv)	
	S6012-A01.020 <sup>(a)</sup> PNL 020 <sup>(b)</sup> Concentration (ppmv)	7 J	S6012-A02.028 <sup>(a)</sup> PNL 028 <sup>(b)</sup> Concentration (ppmv)	7 J	S6012-A03.035 <sup>(a)</sup> PNL 035 <sup>(b)</sup> Concentration (ppmv)	S6012-A12.041 <sup>(a)</sup> PNL 041 <sup>(b)</sup> Concentration (ppmv)	S6012-A26.060 <sup>(a)</sup> PNL 060 <sup>(b)</sup> Concentration (ppmv)	S6012-A12.041 <sup>(a)</sup> PNL 041 <sup>(c)</sup> Concentration (ppmv)		
Hydrogen	4	U	4	U	4	4	4	4	4	U
Methane	380	U	383	U	242	244	236	245	241	U
Carbon Dioxide	3	U	3	U	3	3	3	3	3	U
Carbon Monoxide	2	U	2	U	8	8	7	9	8	J

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 041; results are not included in the calculation of average concentrations.

J = Target compound detected above the Instrument Detection Limit (IDL) but below Estimated Quantitation Limit (EQL).

U = Target compound not detected at or above the IDL.

# **Appendix C**

## **Tank Vapor Characterization: Total Non-Methane Hydrocarbons**

## Appendix C

### Tank Vapor Characterization: Total Non-Methane Hydrocarbons

#### C.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant-free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02<sup>(a)</sup>. The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis. 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 hydrocarbons (TNMHC) 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 TNMHCs 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. 1), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.
  - (b) Pacific Northwest Laboratory. 6/95. *Determination of TO-12 Total Nonmethane Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Flame Ionization Detection*, PNL-TVP-08 (Rev. 0), PNL Technical Procedure, 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 TNMHC is calibrated by using propane as the calibration standard and using that response factor as an external standard method. The instrument calibration mixture for the PNL-TVP-08 analysis consists of National Institute for Standards and Technology (NIST) 99.999% propane analyzed using a five-point, multi-level, linear regression curve.

A 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 TNMHCs. 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:

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

The ng/m<sup>3</sup> concentrations are calculated from mg/m<sup>3</sup> using the equation:

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

#### C.4 Total Non-Methane Hydrocarbons Sample Results

Five SUMMA™ canisters were returned to the laboratory on February 8, 1996, under Westinghouse Hanford Company (WHC) chain-of-custody 100033 (see Appendix D). The samples were analyzed on February 23, 1996.

Table C.1 lists results of the TO-12 gas analysis from samples collected from the headspace of Tank T-104, ambient air collected ~10 m upwind of the tank, and ambient air collected through the vapor sampling system. The concentration in the ambient air samples ranged from 0.21 mg/m<sup>3</sup> to 0.24 mg/m<sup>3</sup>. This concentration was below the method EQL. Therefore, it should be considered only an approximate concentration. Concentrations in the three tank headspace samples ranged from 1.83 mg/m<sup>3</sup> to 2.00 mg/m<sup>3</sup>, with an average concentration of 1.93 mg/m<sup>3</sup>. A replicate analysis was performed on SUMMA™ canister PNL 041; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

**Table C.1.** TO-12 Results for Samples Collected from the Headspace of Tank T-104 and for Ambient Air and Ambient Air Through the VSS Collected near Tank T-104 in SUMMA™ Canisters on 02/07/96

TO-12	Ambient Air		Tank Samples						Average Concentration Tank Samples (mg/m3)
	Upwind	Through VSS	S6-012-A01.020 <sup>(a)</sup>	S6-012-A02.028 <sup>(a)</sup>	S6-012-A03.035 <sup>(a)</sup>	S6-012-A12.041	S6-012-A26.060 <sup>(a)</sup>	S6-012-A12.041 <sup>(a)</sup>	
	PNL 020 <sup>(b)</sup>	PNL 028 <sup>(b)</sup>	PNL 035 <sup>(b)</sup>	PNL 041 <sup>(b)</sup>	PNL 041 <sup>(b)</sup>	PNL 060 <sup>(b)</sup>	PNL 041 <sup>(b)(c)</sup>	PNL 041 <sup>(b)(c)</sup>	PNL 041 <sup>(b)(c)</sup>
	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)	Concentration (mg/m3)
	0.21 J	0.24 J	1.96	2.00	1.83	3.09	1.93		

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 041; results are not included in the calculation of average concentrations.

Data Qualifier Flags

J = Target compound detected above the Instrument Detection Limit (IDL) but below Estimated Quantitation Limit (EQL).

## **Appendix D**

### **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) 373-2891  
Page 85-3152 / FAX 373-3793

Project Designation/Sampling Locations 200 East Tank Farm  
241-T-104 Tank Vapor Sample SAF S6012  
(VSS Truck)

Collection date 02 - 07 - 96  
Preparation date 01 - 26 - 96

Ice Chest No.

Field Logbook No. WHC- N-642.10

Method of Shipment Government Truck

Shipped to PNNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6012 - A04 . 96S *	Collect NH <sub>3</sub> /H <sub>2</sub> O Sorbent Trap #1	Sorbent line 1
S6012 - A05 . 97S *	Collect NH <sub>3</sub> /H <sub>2</sub> O Sorbent Trap #2	Sorbent line 2
S6012 - A06 . 98S ..	Collect NH <sub>3</sub> /H <sub>2</sub> O Sorbent Trap #3	Sorbent line 3
S6012 - A07 . 99S ..	Collect NH <sub>3</sub> /H <sub>2</sub> O Sorbent Trap #4	Sorbent line 4
S6012 - A13 . S01 *	Collect NH <sub>3</sub> /H <sub>2</sub> O Sorbent Trap #5	Sorbent line 1
S6012 - A14 . S02 *	Collect NH <sub>3</sub> /H <sub>2</sub> O Sorbent Trap #6	Sorbent line 2
S6012 - A15 . S03 *	Collect NH <sub>3</sub> /H <sub>2</sub> O Sorbent Trap #7	Sorbent line 3
S6012 - A16 . S04 *	Collect NH <sub>3</sub> /H <sub>2</sub> O Sorbent Trap #8	Sorbent line 4
S6012 - A31 . S05 *	Open, close & store NH <sub>3</sub> /H <sub>2</sub> O field blank #1	In VSS truck
S6012 - A32 . S06 *	Open, close & store NH <sub>3</sub> /H <sub>2</sub> O field blank #2	In VSS truck
S6012 - A33 . S07 *	Open, close & store NH <sub>3</sub> /H <sub>2</sub> O field blank #3	In VSS truck

[ ] Field Transfer of Custody		[ X ] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
G W Dennis <i>G.W. Dennis</i>	01-30-96	1345	J A Edwards <i>J A Edwards</i>	01-30-96	1345
J A Edwards <i>J A Edwards</i>	01-30-96	1435	T B Utech <i>T B Utech</i>	01-30-96	1435
<del>T B Utech / T B Utech</del>	<del>2-8-96</del>	<del>1350</del>	<del>J A Edwards / J A Edwards</del>	<del>2-8-96</del>	<del>1350</del>
<del>J A Edwards / J A Edwards</del>	<del>2-12-96</del>	<del>1330</del>	<del>G.W. Dennis / G.W. Dennis</del>	<del>2-12-96</del>	<del>1330</del>
<del>G.W. Dennis / G.W. Dennis</del>	<del>2-20-96</del>	<del>0830</del>	<del>A.O. Slate / SO Slate</del>	<del>2-20-96</del>	<del>0830</del>

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	
Sorbents shipped on ice? (<10°C)	(Y) N / (Y) N	
Rad release stickers on samples?	(Y) N / (Y) N	
Activity report from 222S?	(Y) N / (Y) N	
COC copy for LRB, RIDS filed?	(Y) N / (Y) N	
COC copy for sorbent follow-on?	(Y) N / (Y) N	Original COC follows sorbent media
	POC <i>(Signature)</i>	POC <i>(Signature)</i>

(Revised 10/31/95 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 85-3152 / FAX 373-3793

Project Designation/Sampling Locations 200 East Tank Farm Collection date 02 - 07 - 96  
241-T-104 Tank Vapor Sample SAF S6012 Preparation date 01 - 29 - 96  
(VSS Truck)

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

S6012 - A01 .020 Ambient Air SUMMA #1 Upwind of T-104  
S6012 - A02 .028 Ambient Air SUMMA #2 Through Port # 15

S6012 - A03 .035 SUMMA #3 Port # 11  
S6012 - A12 .041 SUMMA #4 Port # 13  
S6012 - A26 .060 SUMMA #5 Port # 15

[ ] Field Transfer of Custody		[ X ] Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
J A Edwards / J A Edwards	01-30-96	1435	T.B. Utell / T.B. Utell	01-30-96	1435	
T.B. Utell / T.B. Utell	2-8-96	1350	J A EDWARDS / J A Edwards	2-8-96	1350	

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 / Y/N	
Activity report from 222S?	Y/N / Y/N	
COC copy for LRB, RIDS filed?	Y/N / Y/N	
	POC (Signature)	POC (Signature)

(Revised 10/31/95 PNNL)

**Distribution List**

**PNNL-11165**

**PNNL**

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

**Lockheed**

Larry Pennington	S7-21
Luther Buckley	R2-12

**DOE-RL**

Carol Babel	S7-54
Jim Thompson	S7-54