Pacific Northwest National Laboratory

Operated by Battelle for the
U.S. Department of Energy

TANK VAPOR CHARACTERIZATION PROJECT

Tank 241-BX-106 Headspace Gas and Vapor Characterization Results from Samples Collected on August 15, 1996

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August 1997

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Prepared for Lockheed Martin Hanford
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Contract DE-AC06-76RLO 1830

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PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

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Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
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Summary

This report presents the results from analyses of samples taken from the headspace of waste storage tank 241-BX-106 (Tank BX-106) at the Hanford Site in Washington State. Tank headspace samples collected by Westinghouse Hanford Company (WHC) were analyzed by Pacific Northwest National Laboratory (PNNL) to determine headspace concentrations of selected non-radioactive analytes. Analyses were performed by the Vapor Analytical Laboratory (VAL) at PNNL. Vapor concentrations from sorbent trap samples are based on measured sample volumes provided by WHC.

No analytes were determined to be above the immediate notification limits specified by the sampling and analysis plan (SAP, Buckley 1996). Ammonia was the principal flammable constituent of the Tank BX-106 headspace, determined to be present at approximately 0.031% of its lower flammability limit (LFL). Total headspace flammability was estimated to be <0.143% of the LFL.

Average measured concentrations of targeted gases, inorganic vapors, and selected organic vapors are provided in Table S.1. A summary of experimental methods, including sampling methodology, analytical procedures, and quality assurance and control methods are presented in Section 2.0. Detailed descriptions of the analytical results are provided in Section 3.0.

Table S.1. Average Measured Concentrations of Gases and Inorganic and Organic Vapors in Tank BX-106 Sampled on 8/15/96

<u>Category</u>	<u>Sample Medium</u>	<u>Analyte</u>	<u>Concentration^(a)</u>	<u>Units</u>
Inorganic Vapors	Sorbent Traps	Ammonia	47	ppmv
		Nitric Oxide (NO)	<0.16	ppmv
		Nitrogen Dioxide (NO ₂)	<0.16	ppmv
		Water	10.3	mg/L
Permanent Gases	SUMMA™ Canisters	Hydrogen	<17	ppmv
		Methane	<25	ppmv
		Carbon Dioxide	<17	ppmv
		Carbon Monoxide	<17	ppmv
		Nitrous Oxide (N ₂ O)	44	ppmv
Total Non-Methane Organic Compounds	SUMMA™ Canisters	Total Non-Methane Organic Compounds	1.95	mg/m ³
Flammables	SUMMA™ Canisters and Sorbent Traps	Flammables	<0.143	% LFL

(a) Concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data from three samples. Mass concentrations are at reference temperature and pressure of 0°C and 1.013 bar.

Acknowledgments

The authors gratefully acknowledge the support of other project staff at PNNL who contributed to the successful completion of this sampling and analysis activity. S. O. Slate, K. P. Schielke, L. M. P. Thomas, and G. W. Dennis supported inorganic laboratory work.

Terms and Abbreviations

% D	% Difference
CCV	continuing calibration verification
COC	chain-of-custody
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
ICV	initial calibration verification
ISVS	In Situ Vapor Sampling System
LFL	lower flammability limit
NIST	National Institute for Standards and Technology
OSHA	Occupational Safety and Health Administration
PNL	Pacific Northwest Laboratory (previous name for the 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
SAP	sample and analysis plan
SCIC	suppressed-conductivity ion chromatography
SIE	selective ion electrode
SRM	standard reference material
STP	standard temperature and pressure
SUMMA™	process for passivating stainless steel
TEA	triethanolamine
TNMOC	total non-methane organic compound
UHP	ultra high purity
VAL	Vapor Analytical Laboratory
WHC	Westinghouse Hanford Company

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1.0 Introduction

This report presents results of chemical analyses of vapor samples collected by WHC on August 15, 1996 from the headspace of waste storage tank 241-BX-106 (Tank BX-106) at the Hanford Site in Washington State. Pacific Northwest National Laboratory^(a) provided SUMMA™ canisters and sorbent traps for sample collection, and analyzed the samples according to instructions in the SAP (Buckley 1996). Analytical work was performed by the PNNL VAL in the 300 Area of the Hanford Site under the PNNL Tank Vapor Characterization Project.

Pacific Northwest National Laboratory provided six sets of sorbent traps for selected inorganic analytes (four samples and two field blanks) and five SUMMA™ canisters for permanent gases and organic analytes (three headspace samples and two ambient air samples). Sample devices and controls were provided to WHC on August 7, 1996, and returned to PNNL on August 26, 1996. Westinghouse Hanford Company measured and reported to PNNL the sample volumes needed to determine headspace concentrations from sorbent trap samples.

Specific analytical methods for sample analysis are described in Section 2.0. Results and known sampling and analytical variances from established quality assurance (QA) requirements, where significant, are documented in Section 3.0. Chain-of-custody forms used to document possession and transfer of samples and controls are provided in Appendix A.

^(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. The former name is used when previously published documents are referenced.

2.0 Analytical Methods

Table 2.1 summarizes the analytes, sampling media, analytical methods, and laboratory procedures. Table 2.2 summarizes information regarding sample media, handling, and storage procedures.

Table 2.1. Sampling and Analysis Methods Summary

<u>Analyte</u>	<u>Sampling Media</u>	<u>Extraction Method</u>	<u>Analysis Method</u>	<u>Procedure</u>
Ammonia	Acidified carbon bead sorbent trap	Aqueous extraction	SIE analysis	PNL-ALO-226
Nitric Oxide and Nitrogen Dioxide	Triethanolamine impregnated sorbent traps	Aqueous extraction	IC	PNL-ALO-212
Water Vapor	Other inorganic sorbent traps + silica gel sorbent trap	None	Gravimetric analysis (sample weight gain)	PNL-TVP-09
Carbon Monoxide, Carbon Dioxide, Hydrogen, Methane, and Nitrous Oxide	SUMMA™ canisters	Analysis of SUMMA™ canister subsample	GC/TCD	PNL-TVP-05
Total Non-Methane Organic Compounds	SUMMA™ canisters	Cryo-focusing of SUMMA™ canister subsample	GC/FID	PNL-TVP-08

Table 2.2. Sample Media Preparation, Handling, and Storage

<u>Sampling Media</u>	<u>Supplier and Catalog Number</u>	<u>Preparation Procedure</u>	<u>Handling and Storage Procedure</u>
Inorganic vapor sorbent traps	SKC No. 226-29 SKC No. 226-40-02 SKC No. 226-10-04	PNL-TVP-09	PNL-TVP-07
SUMMA™ canisters	Scientific Instrumentation Specialist	PNL-TVP-02	PNL-TVP-07

2.1 Inorganic Vapors

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to WHC for sampling the tank headspace. Blanks, and exposed samples were returned to PNNL for analysis. Analyses were performed to provide information on the tank-headspace concentration of the following analytes: ammonia, nitrogen dioxide (NO₂), nitric oxide (NO), and water. Samples were prepared, handled, and disassembled as described in Technical Procedure PNL-TVP-09^(a).

2.1.1 Sampling Methodology

Standard glass tubes containing sorbent materials to trap ammonia, NO, NO₂, and water vapors were obtained, prepared, and submitted for vapor sampling. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration (OSHA) to perform workplace monitoring and because of available procedures and verification results associated with that particular application. Each sorbent trap contained two sorbent sections separated by a glass wool plug. Sorbent media in the two sections were segregated and analyzed separately (except for analysis for water). Analyses of the second sorbent (breakthrough) sections were performed to demonstrate complete collection of the target analyte by the first sorbent section.

The ammonia 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 ammonia was chemisorbed as ammonium sulfate [(NH₄)₂SO₄]. The NO₂ traps contained a zeolite impregnated with triethanolamine (TEA), with 400 mg in the primary and 200 mg in the breakthrough sections. The NO₂ was absorbed and disproportionated to equi-molar quantities of nitrite ions (NO₂⁻) and nitrate ions (NO₃⁻). Glass tubes containing 800 mg of an oxidant were used to convert NO to NO₂. The converted NO was then collected as nitrite and nitrate in an NO₂ trap. The water traps contained a total of 450 mg of silica gel. All sorbent traps for a given analyte were from a single manufacturer's batch.

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 trains configured so sample air flow passed in order through the ammonia, nitrogen dioxide, oxidizer, nitric oxide, and desiccant traps. Traps were weighed and then connected to each other using uniform lengths of 3/8-in. perfluoroalkoxy-grade (PFA) Teflon® tubing. The perfluoroalkoxy-grade tubing was heated in hot air and forced over the open ends of the traps to form a tight seal. The inlets of the sorbent trains each consist of a short section of tubing having a 3/8-in. stainless steel Swagelok® nut, and sealed using a Swagelok® cap. The trailing ends of the sorbent trains were each sealed with red plastic caps provided by the manufacturer.

^(a) 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, Richland, Washington.

2.1.1.1 Concentration Calculations. Concentration, in parts per million by volume (ppmv), was determined by dividing the amount of analyte, in μmol , by the moles of the dried tank air sampled. For example, the concentration of a 3.00-L sample containing 75.0 μg of ammonia equals

$$\frac{(75.0 \mu\text{g})(22.4 \text{ L/mol})}{(17.0 \mu\text{g}/\mu\text{mol})(3.00 \text{ L})} = 32.9 \text{ ppmv} \quad (2.1)$$

Measured sample volumes were specified by WHC at standard temperature and pressure (STP; 0°C, 1.013 bar). Because water vapor is removed as an analyte before the sample air stream passes through the mass flow meters, sample volumes exclude water vapor.

2.1.2 Analytical Procedures

2.1.2.1 Ammonia Analysis. The sorbent material from the ammonia traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing breakthrough-section sorbent material were treated with 5.0 mL of DIW. Ammonia present was measured using the selective ion electrode (SIE) procedure PNL-ALO-226^(a). Briefly, the method includes 1) preparing a 1000- $\mu\text{g}/\text{mL}$ ammonia stock standard solution from dried reagent-grade NH_4Cl and DIW, 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100- $\mu\text{g}/\text{mL}$ ammonia 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 ammonia concentration data obtained for the set of working standards, 4) performing a calibration-verification check, using a mid-range dilution of a certified National Institute for Standards and Technology (NIST)-traceable 0.1 M NH_4Cl standard from an independent source, at a minimum of once per batch, 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 signal measurements obtained for samples are compared to those for standards, to determine ammonia concentration in the samples.

2.1.2.2 Nitrite Analysis. The sorbent material for NO_2 and NO traps were desorbed in an aqueous TEA and n-butanol solution and analyzed by suppressed-conductivity ion chromatography (SCIC) for nitrite according to PNL-ALO-212, Rev. 1^(b) modified to obviate interferences by concentrations of non-target analytes. Specifically, the modifications used were 1) eluent 1.44 mM Na_2CO_3 + 1.8 mM NaHCO_3 at 2.0 mL/min, 2) one guard column (AG4A) and two separator columns (AS4A) in series instead of just one separator column, and 3) all standards, samples, and blanks injected into the sample loop through 0.45- μm syringe filters.

Primary and breakthrough section materials were analyzed separately using identical procedures. Each analytical session was conducted as follows. Working nitrite standards were prepared by diluting a stock nitrite standard with desorbing solution. An initial calibration curve was

(a) Procedure entitled "Ammonia (Nitrogen) in Aqueous Samples," PNL-ALO-226 Rev. 0, in the *Analytical Chemistry Laboratory (ACL) Procedure Compendium*, Vol. 3: Inorganic Instrumental Methods. Pacific Northwest National 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.

prepared from the instrument response versus nitrite standard concentration data for the set of working standards. A calibration verification check using one of the midrange standards was performed at a minimum of once per batch. If the instrument response indicated that sample nitrite concentration was outside the calibration range, 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. Instrument responses observed for samples were compared to those for standards to determine the nitrite concentration of the samples. Because the analytes were collected on the sorbent as equal quantities of nitrite and nitrate, and the analysis was specific for nitrite, the moles of NO₂ and NO were determined by doubling the analytically determined moles of nitrite.

2.1.2.3 Water Analysis. All sorbent traps used to make each multi-trap 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. Mass gain was assumed to be entirely due to collection of water vapor. Field blanks were used to correct results.

2.1.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in PNL-ALO-212, PNL-ALO-226, and Quality Assurance Plan ETD-002. Estimated quantitation limits (EQLs) for the inorganic vapors are given in Table 2.3.

The accuracy of concentration measurements depends on errors associated with both sampling and analysis. Ammonia results were estimated to be within 5% of their true values. 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 NO₂ and NO) are performed using certified but not NIST-traceable SRM; this is because NIST does not make a nitrite SRM. Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for ammonia above, the estimated maximum bias for NO₂ results is $\pm 10\%$, and for NO results it is $\pm 5\%$.

Table 2.3 Quantitation Limits for Selected Inorganic Analytes

<u>Analyte</u>	<u>Formula</u>	<u>EQL^(a)</u> <u>(ppmv)</u>
Ammonia	NH ₃	0.71
Nitrogen Dioxide	NO ₂	0.16
Nitric oxide	NO	0.16
Mass (water) ^(b)	n/a	0.3 mg/L

(a) The lowest calibration standard is defined as the EQL.

(b) The vapor-mass concentration, thought to be largely water vapor, is determined gravimetrically.

n/a = not applicable.

The accuracy of measurements of sample mass is typically ± 0.1 mg, or 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 multi-trap trains, is determined for each sample job and is typically about ± 1 mg per five-trap sorbent train.

2.2 Permanent Gases

SUMMA™ canister samples were analyzed for carbon dioxide, carbon monoxide, hydrogen, methane, and nitrous oxide (N₂O).

2.2.1 SUMMA Canister Preparation

All SUMMA™ canisters are cleaned and verified contaminant-free according to PNNL Technical Procedure PNL-TVP-02^(a) before use. The cleaning procedure uses an EnTech 3000 cleaning system that alternately fills the canisters with purified humid air and evacuates them for several cycles while the canister is heated. If the canister is verified as clean, the canister is evacuated to 5 mtorr and tagged. Before sending the canisters to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 μ L of distilled water and labeled. 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. All canisters are stored at room temperature.

2.2.2 Analytical Procedure

The SUMMA™ canister samples were analyzed for five permanent gases by gas chromatography/thermal conductivity detection (GC/TCD). Aliquots of sampled air (undiluted) are drawn directly from each SUMMA™ 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 carbon monoxide, carbon dioxide, N₂O, and methane using helium as the carrier gas. A second GC/TCD analysis is performed for hydrogen 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 EQLs are listed in Table 2.4.

^(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.

Table 2.4 Quantitation Limits for Permanent Gases

<u>Analyte</u>	<u>Formula</u>	<u>EQL (ppmv)</u>
Carbon Dioxide	CO ₂	17
Carbon Monoxide	CO	17
Methane	CH ₄	25
Hydrogen	H ₂	17
Nitrous Oxide	N ₂ O	17

2.2.3 Quality Assurance/Quality Control

Standards for the permanent gas analyses were blended from commercially prepared and certified standards. The instrument was calibrated at five different concentrations for methane over a range of 25 to 2100 ppmv, calibrated for carbon monoxide, carbon dioxide, and N₂O over a range of 17 to 2100 ppmv, and calibrated for hydrogen over a range of 17 to 2120 ppmv. An average response factor from the calibration was used for quantification.

Each analyte was quantitated by comparison of sample analyte peak area to the calibration plot generated for the compound. The 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.

2.3 Total Non-Methane Organic Compounds

2.3.1 Analytical Procedure

SUMMA™ canister samples were analyzed for total non-methane organic compounds (TNMOCs) according to PNNL Technical Procedure PNL-TVP-08^(a), which is similar to U.S. Environmental Protection Agency (EPA) Task Order 12 (TO-12). Twenty-four hours before analysis, SUMMA™ canister samples are pressurized with purified air (Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The original pressure is first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level exactly twice the original pressure.

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 into the GC/FID. 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.

(a) Pacific Northwest National 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, Richland, Washington.

Concentration in mg/m^3 was derived from the 10-point multilevel calibration curve from the propane standard using the following equation:

$$\text{mg}/\text{m}^3 = \frac{(\text{ng TNMOC}) \times (\text{dilution factor})}{\text{mL sampled volume}} \quad (2.2)$$

2.3.2 Quality Assurance/Quality Control

The TNMOC is calibrated by using propane as the calibration standard. The instrument calibration mixture for the TNMOC analysis consists of NIST 99.999% propane analyzed using a 10-point, multilevel, linear regression curve.

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 either 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 analysis of purified air must be below $0.1 \text{ mg}/\text{m}^3$. Second, an instrument continuing calibration run using 100-mL UHP propane followed by one blank volume of Aadco air.

3.0 Analysis Results

Results from the sampling of the headspace of Tank BX-106 on August 15, 1996 (Sample Job S6082) are provided below.

3.1 Inorganic Vapors

Measured vapor concentrations of ammonia, nitric oxide (NO), nitrogen dioxide (NO₂), and water are given in Table 3.1. The vapor concentration results were based on four samples for each compound. The four inorganic vapors were collected at the same time using sorbent traps connected in series. Sample air was drawn first through an ammonia trap, then through a three-tube system that collected nitrogen dioxide and nitric oxide (described below), and then through a desiccant trap to remove any remaining water vapor.

Two field blank multi-trap trains, identical to sample multi-trap trains discussed in Section 2.1, were included in the tube bundle lowered into the headspace of Tank BX-106 during sample job S6082. No air was pulled through these field blank multi-trap trains. Any analyte found in the field blank multi-trap trains over and above levels in unexposed tubes was attributed to passive sampling. Data in Table 3.1 have been corrected for these minor effects of passive sampling.

Results provided in Table 3.1 are estimated to be accurate to within $\pm 10\%$ and within the $\pm 30\%$ specified by the SAP. Percent relative standard deviations of the measured concentrations were $<9\%$, which is within the 25% specified by the SAP.

3.1.1 Ammonia

Ammonia analyses were performed on September 3, 1996, 19 days after sample collection and within established holding times (Ligotke et al. 1995). All samples (100%) were successfully analyzed, and no deviations from the procedure were noted.

The blank-corrected ammonia quantities in the sorbent traps ranged from 3.45 to 4.25 μmol in front sections; blank corrected back sorbent section ammonia concentrations were $<0.01 \mu\text{mol}$. Blank corrections of 0.13 μmol in front and 0.07 μmol in the back sections, were about 3.3% of collected quantities. The analysis of one sample was a duplicate and indicated a reproducibility of $\pm 0.3\%$. One blank sorbent trap was spiked with 17 ppm of ammonia and yielded a percentage recovery of 104%. One sample leachate was spiked after initial analysis with approximately twice the quantity of ammonia in the sample and yielded a percentage recovery of 99%. The initial and continuing calibration verification (ICV, CCV) standards, using NIST-traceable material, yielded percentage recoveries of 99% (ICV) and 101% and 102% (CCV) during the analytical session. A five-point calibration was performed over an ammonia range of 0.1 to 100 $\mu\text{g/ml}$.

3.1.2 Nitric Oxide and Nitrogen Dioxide

Nitric oxide and nitrogen oxide analyses were performed on September 4, 1996, 20 days after sample collection, and within established holding times (Ligotke et al. 1995). All samples (100%) were successfully analyzed. No deviations from the procedure were noted.

Blank-corrected NO_2^- quantities in the sorbent traps were all $<0.013 \mu\text{mol}$. Nitrite blank levels used to correct data were $0.0059 \mu\text{mol}$ in front (four of four blanks analyzed) and $0.0037 \mu\text{mol}$ in back (two of four blanks analyzed) sorbent sections. The analyses of two samples were duplicated and yielded repeatabilities of $\pm 1.4\%$ and $\pm 0.8\%$. Two sample leachates were spiked with 0.125 and $0.25 \text{ ppm } \text{NO}_2^-$ and yielded percentage recoveries of 85% and 97% , respectively. A 4-point calibration was performed over a concentration range of 0 to $0.5 \mu\text{g/mL } \text{NO}_2^-$ in the desorbing matrix.

3.1.3 Water

Analyses for water vapor were performed on August 27, 1996, 12 days after sample collection and within established holding times (Ligotke et al. 1995). All samples (100%) were successfully analyzed.

All multi-trap sample mass gain is assumed to be due to adsorption of water. This is justified because the total mass concentration of other vapors in the headspace of Hanford waste tanks are typically two to three orders of magnitude less than the mass concentration of the water vapor found in even relatively dry tanks. Water vapor concentrations are given in Table 3.1 for both dry air at STP (0°C and 1.013 bar) and for moist air at tank conditions. Because the sample volumes were measured after all water vapor was removed by the sorbent traps, the measured sample volumes are for dry air. The average water vapor concentration was 10.3 mg of water per L of dry air at STP. The result was determined from an average mass gain of 23.6 mg from all four multi-trap trains. The blank correction applied to the results was -4.4 mg per multi-trap train. A control mass was measured and indicated a measurement accuracy of $\pm 0.1 \text{ mg}$. The average water vapor concentration corresponds to a tank headspace dew point at 10.3°C and relative humidity at 56% at the time of sampling.

3.2 Permanent Gases

Hydrogen analyses were performed on September 12, 1996, and analyses for other permanent gases were performed on September 13, 1996. All analyses were conducted within the 60-day administrative holding time as specified in the WHC Tank Vapor Characterization QA Plan (WHC 1994). All samples (100%) were successfully analyzed and used in the averages. No deviations from standard procedures were noted.

Measured concentrations of carbon monoxide, carbon dioxide, hydrogen, methane, and N_2O are provided in Table 3.2. Results were based on three samples for each compound. Nitrous oxide at an average concentration of 44 ppmv was the only permanent gas detected in Tank BX-106. The relative percent difference (RPD) between duplicate analyses of a single SUMMA™ canister was 2% for nitrous oxide.

Results provided in Table 3.2 are estimated to be accurate to within $\pm 30\%$ as specified by the SAP.

3.3 Total Non-Methane Organic Compounds

Analyses for TNMOCs were performed on September 25 and 26, 1996, which is within the 60-day administrative holding time as specified in the WHC Tank Vapor Characterization QA Plan (WHC 1994). All three tank samples and the two ambient samples (100%) were successfully analyzed and used in the averages.

Table 3.3 lists results of the EPA TO-12 analysis of SUMMA™ canister samples for TNMOCs. Results in Table 3.3 are reported in two different units; in the upper row the mass concentration (mg/m^3) of non-methane organic compounds is given at STP (0°C and 1.013 bar), and in the lower row, by EPA TO-12 convention, as ppmv of carbon based on propane as the standard. The average concentration in the three tank headspace samples was $1.95 \text{ mg}/\text{m}^3$ or 0.82 ppmv of carbon. Results provided in Table 3.3 are estimated to be accurate to within $\pm 30\%$ as specified by the SAP. The RPD for duplicate analysis of a single SUMMA™ canister was 3%.

3.3.1 Procedural Deviations, Observations, and Anomalies

A deviation was made to the current procedure and documented in Vapor Deviation Report JAE082996. In accordance with the current method, past TO-12 analyses used a calibration method based on an average response factor spanning the full dynamic range. Because the low level standards are impacted to some extent by the small amount of system blank present, the average response factor method generates an apparent non linearity introducing an unnecessary amount of level dependent error. To correct this situation, data included in the August 20, 1996 and all subsequent calibrations shall use a linear regression fit which includes both a slope and intercept. The correlation coefficient for the August 20, 1996 ten point calibration curve was 0.99996, an extremely well ordered data set. A new revision of PNL-TVP-08 currently under preparation will reflect this amendment.

3.4 Flammability

The analytical results presented above can be used to estimate the tank BX-106 headspace flammability at the time of sampling. Flammability is calculated using the ammonia concentration from the inorganic analysis, carbon monoxide, hydrogen, and methane concentrations measured from the permanent gas analysis, and the total nonmethane hydrocarbon concentration determined from the TO-12 analysis. Table 3.4 summarizes the calculated flammability data. Ammonia was the principle flammable constituent of the Tank BX-106 headspace, determined to be present at approximately 0.031% of its LFL. Total headspace flammability was estimated to be $<0.143\%$ of the LFL.

Table 3.1 Inorganic Vapor Concentrations from Tank BX-106 Sampled on 8/15/96

Analyte	CAS Number	S6082-A07-70R	S6082-A08-71R	S6082-A09-73R	S6082-A10-74R	Average	Standard Deviation
Ammonia (ppmv)	7664-41-7	51	42	47	47	47	4.0
Nitric Oxide (ppmv)		<0.16	<0.16	<0.16	<0.16	<0.16	
Nitrogen Dioxide (ppmv)		<0.16	<0.16	<0.16	<0.16	<0.16	
Water ^(a) (mg/L)		9.8	11.0	9.3	11.2	10.3	0.9
Water ^(b) (mg/L)		8.9	9.9	8.4	10.1	9.3	0.8

Footnotes

(a) Dry air at 0°C and 1.013 bar.

(b) Moist air at tank temperature and pressure.

Table 3.2 Permanent Gas Analysis Results from Tank BX-106 Sampled on 8/15/96

Permanent Gas Analyte	Ambient Air Upwind	Ambient Air Through Bundle	Tank Samples				Relative Percent Difference of Duplicate Analysis %	Mean (ppmv)	Standard Deviation
	S6082-A01.024 ^(a) PNL 024 ^(b) Concentration (ppmv)	S6082-A02.027 ^(a) PNL 027 ^(b) Concentration (ppmv)	S6082-A04.138 ^(a) PNL 138 ^(b) Concentration (ppmv)	S6082-A05.164 ^(a) PNL 164 ^(b) Concentration (ppmv)	S6082-A06.229 ^(a) PNL 229 ^(b) Concentration (ppmv)	S6082-A05.164 ^{(a)(c)} PNL 164 ^(b) Concentration (ppmv)			
Hydrogen	<17	<17	<17	<17	<17	<17	na	<17	
Methane	<25	<25	<25	<25	<25	<25	na	<25	
Carbon Dioxide	431	383	<17	<17	<17	<17	na	<17	
Carbon Monoxide	<17	<17	<17	<17	<17	<17	na	<17	
Nitrous Oxide	<17	<17	44	44	43	44	2	44	1

Footnotes

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 171; results are not included in the calculation of average concentrations.

na Not Applicable

Table 3.3 Total Non-Methane Organic Compound Analysis Results from Tank BX-106 Sampled on 8/15/96

	Ambient Air Upwind	Ambient Air Through Bundle	Tank Samples				Relative Percent Difference of Duplicate Analysis		
	S6082-A01.024 ^(a)	S6082-A02.027 ^(a)	S6082-A04.138 ^(a)	S6082-A05.164 ^(a)	S6082-A06.229 ^{(a)(c)}	S6082-A05.164 ^(a)	%	Mean	St. Dev
	PNL 024 ^(b)	PNL 027 ^(b)	PNL 138 ^(b)	PNL 164 ^(b)	PNL 229 ^(b)	PNL 164 ^{(b)(c)}			
	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration			
TO-12 (mg/m ³)	<0.59	<0.59	1.92	1.87	2.07	1.82	3	1.95	0.10
Total Carbon (ppm)								0.82	

Footnotes

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 164; results are not included in the calculation of average concentrations.

Table 3.4 Flammability Data for Tank BX-106 Sampled on 8/15/96

Analyte	CAS #	Lower Flammability Limit(LFL)	Average Measured Concentrations	% of LFL ^(a)
Ammonia (ppm)	7664-41-7	150000	47	0.031
Carbon Monoxide (ppm)	630-08-0	125000	<17	<0.014
Hydrogen (ppm)	1333-74-0	40000	<17	<0.043
Methane (ppm)	74-82-8	50000	<25	<0.05
TNMOC (mg/m ³)		42000	1.95	0.005
Total				<0.143

(a) Less than values are calculated using the average concentration less than values.
These values are summed to determine the total LFL.

4.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank BX-105 on August 15, 1996 (Sample Job S6082). 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 (Buckley 1996). 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 (Buckley 1996).

5.0 References

Buckley, L. L. 1996. *Vapor Sampling and Analysis Plan*. WHC-SD-WM-TP-335, Rev. 2C, Westinghouse Hanford Company, Richland, Washington.

Ligotke, M. W., J. S. Fruchter, J. L. Huckaby, M. B. Birn, B. D. McVeety, J. C. Evans, K. H. Pool, K. L. Silvers, and S. C. Goheen. 1995. *Waste Tank Vapor Characterization Project: Annual Status Report for FY 1995*. Pacific Northwest National Laboratory, Richland, Washington.

Pacific Northwest National Laboratory. *Analytical Laboratory Procedure Compendium*. Procedure PNL-ALO-271. PNL-MA-599, Pacific Northwest National 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. 1, Pacific Northwest National Laboratory, Richland, Washington.

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

Westinghouse Hanford Company (WHC). 1994. *Quality Assurance Project Plan for Tank Vapor Characterization*. WHC-SD-WM-QAPP-013, Rev. 2, Westinghouse Hanford Company, Richland, Washington.

Appendix A

Chain-of-Custody Sample Control Forms

Custody Form Initiator

J. A. Edwards - PNNL

Telephone (509) 373-0141

Page 85-3009 / FAX 376-2329

Company Contact

R. D. Mahon - WHC

Telephone (509) 373-2891

Page 85-3656 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm
241-BX-106 Tank Vapor Sample SAF S6082
(ISVS Cart)

Collection date 08 - 15 - 96

Preparation date 08 - 01 - 96

Ice Chest No.

Field Logbook No. WHC-N-647-8

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

S6082 - A01 . 024 Collect Ambient Air Sample SUMMA #1
S6082 - A02 . 027 Collect Ambient Air Sample SUMMA #2 (through tube bundle)

S6082 - A04 . 138 Collect SUMMA #3
S6082 - A05 . 164 Collect SUMMA #4
S6082 - A06 . 229 Collect SUMMA #5

☐ Field Transfer of Custody			☒ Chain of Possession			(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time			
J L Julia	08-7-96	1020	ES MATT S/James	08-07-96	1220			
ES MATT S/James	8/26/96	1050	GS CAPRIO / JLD Call	8/26-96	1050			
GS CAPRIO / JLD Call	8/26/96	1355	J A EDWARDS	8/26/96	1355			

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/release? (a ≤100/B ≤400 pCi/g)	☒ Y/N	
☒ COC copy for LRB, RIDS filed?	☒ Y/N	

POC

POC

(WHC-SD-WM-TP-335, REV. 2, Table 2b)

(Revised 05/30/96 PNNL)

Distribution List

PNNL-11458

PNNL

J. C. Evans	K6-96
K. H. Pool	P8-08
B. L. Thomas	K4-13
K. B. Olsen	K6-96
A. V. Mitroshkov	K6-96
J. A. Edwards	P8-08
J. L. Julya	K6-75
B. M. Thornton	K6-80 (3 copies)
J. S. Fruchter	K6-96
K. L. Silvers	K9-08
J. L. Huckaby	K6-80
D. A. Varley	K1-06

LMHC

L. D. Pennington	S7-21
L. L. Buckley	R2-12

DOE-RL

C. A. Babel	S7-54
J. F. Thompson	S7-54