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TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank 241-C-202: Results from Samples Collected on 06/25/96

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Prepared for Westinghouse Hanford Company
under a Related Services Agreement
with the U.S. Department of Energy
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Summary

This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-C-202 (Tank C-202) 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 organic compounds 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 C-202 on 6/25/96

Category	Sample Medium	Analyte	Vapor[a] Concentration	Units
Inorganic Analytes[b]	Sorbent Traps	NH_3	< 0.71	ppmv
		NO_2	< 0.16	ppmv
		NO	< 0.16	ppmv
		H_2O	7.9 ± 0.3	mg/L
Permanent Gases	SUMMA™ Canister	CO_2	402	ppmv
		CO	< 17	ppmv
		CH_4	< 25	ppmv
		H_2	< 17	ppmv
		N_2O	< 17	ppmv
Total Non-Methane Organic Compounds (TO-12)	SUMMA™ Canister	Non-Methane Organic Compounds	1.23	mg/m^3

(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.

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

CCV	continuing calibration verification
COC	chain-of-custody
C_v	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
ICV	initial calibration verification
IDL	instrument detection limit
ISVS	In Situ Vapor Sampling
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	parts per million by volume
QA	quality assurance
RSD	relative standard deviation
SAP	sample and analysis plan
SCIC	suppressed-conductivity ion chromatography
SRM	standard reference material
SUMMA™	stainless steel, passivated interior canister
TEA	triethanolamine
TNMOC	total non-methane organic compounds
UHP	ultra high purity
VAL	Vapor Analytical Laboratory
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-C-202 (Tank C-202) at the Hanford Site in Washington State. Pacific Northwest National Laboratory (PNNL)[a] contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and analyze samples for inorganic and organic analytes collected from the tank headspace and ambient air near the tank. The analytical work was performed by the PNNL Vapor Analytical Laboratory (VAL) by the Tank Vapor Characterization Project. Work performed was based on a sample and analysis plan (SAP) prepared by WHC. The SAP provided job-specific instructions for samples, analyses, and reporting. The SAP for this sample job was "Vapor Sampling and Analysis Plan" (Homi 1995), and the sample job was designated S6066. Samples were collected by WHC on June 25, 1996, using the In Situ Vapor Sampling System (ISVS).

Sampling devices and controls provided for this job included six sorbent trains for selected inorganic analytes (four sample trains and two field blanks) and five SUMMA™ canisters for permanent gases and total non-methane organic compounds (three sample and two ambient canisters). The samples and controls were provided to WHC on June 24, 1996. Exposed samples and controls were returned to PNNL on July 10 and August 12, 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[b], and upon return to PNNL, were logged into PNNL Laboratory Record Book 55408. Samples were stored at the VAL under conditions (e.g., ambient, refrigerated) required by technical procedures. Access to the samples was controlled and limited to PNNL staff trained in the application of specific technical procedures to handle samples for the tank vapor characterization project. Analyses were performed in the 300 Area at Hanford; specific analytical methods are described in the text. In summary, sorbent traps for inorganic analytes were either weighed (for water analysis) or weighed and desorbed with the appropriate aqueous solutions for analyzing inorganic analytes by either selective electrode or ion chromatography (IC).

Tank headspace canister samples were analyzed for

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

(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. 2, December 1995, *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 C-202 on June 25, 1996, (Sample Job S6066) 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.

SUMMA™ canisters for Tank C-202 were received from WHC with radiation concerns. In order to demonstrate that the tank samples did not exceed radiation limit criteria, SUMMA™ canister PNL 128 was attached to SUMMA™ canister PNL 011. The contents of PNL 128 were allowed to equilibrate through a filter and into PNL 011. The filter was measured and the results verified that the SUMMA™ canisters were below the radiation limit criteria. The SUMMA™ canister samples were radiologically released to the VAL on September 13, 1996.

2.1 Inorganic Analytes

The vapor concentrations of selected inorganic analytes (NH_3, NO_2, and NO) and vapor mass concentration (primarily H_2O) were determined. The average and one standard deviation of concentration results from inorganic sorbent sample trains used to sample headspace vapors were <0.71 ppmv (NH_3), < 0.16 ppmv (NO_2), < 0.16 ppmv (NO), and 7.9 ± 0.3 mg/L (primarily H_2O). The vapor concentration results were based on four samples for each compound. All samples (100%) were successfully analyzed and used in the averages. Representative field blanks were also analyzed and used to correct data.

Results provided above are estimated to be accurate to within $\pm$ 10% (assuming negligible error in the sample volume measurements) and are within the $\pm$ 30% specified by the SAP. Measurement precision, as indicated by the relative standard deviation, was 5% for the compounds found to be present at concentrations greater than the analytical method estimated quantitation limit (EQL), and within the 25% specified by the SAP. These uncertainties were confirmed by evaluation of spikes and continuing calibration standards (NH_3 and NO^-_2) and evaluation of the variability of field blanks (H_2O). All samples were analyzed within 27 days after being collected. No deviations from standard procedures were noted. Data and additional information on samples, analyses, and results are described in Appendix A. The chain-of-custody form used to control samples, 100246, is included in Appendix D.

2.2 Permanent Gases

The complete results of the permanent gas analysis of Tank C-202 can be found in Appendix B. In summary, carbon dioxide at 402 ppmv was the only permanent gas observed above the method EQL in the tank headspace samples.

2.3 Total Non-Methane Organic Compounds

The complete results of the TO-12 analysis of Tank C-202 can be found in Appendix C. In summary, the average concentration in the three tank headspace samples was 1.23 mg/m^3. This concentration was below the cutoff value of 5.0 mg/m^3 set forth by WHC. Therefore, no organic speciation analysis was conducted on the tank headspace samples.

3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank C-202 collected on June 25, 1996 (Sample Job S6066). 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. Known sampling and analytical variances from established QA requirements, where significant, were documented in this report, as required by the SAP (Homi 1995). No immediate notifications were provided because analytical results indicated no specific analytes exceeded the notification levels; notification levels and notification procedures are described in the SAP (Homi 1995).

4.0 Reference and Further Reading

Reference

Homi, C.S. 1995. *Vapor Sampling and Analysis Plan.* WHC-SD-WM-TP-335, Rev. 2A, 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. 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, 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 In Situ Vapor Sampling System (ISVS). Blanks, spiked blanks (when requested), and exposed samples were returned to Pacific Northwest National Laboratory (PNNL) for analysis. Analyses were performed to provide information on the tank headspace concentration of the following analytes: ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_2O). Procedures were similar to those developed previously during sample jobs performed with the ISVS 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 NH_3 and mass. Samples were prepared, handled, and disassembled as described in Technical Procedure PNL-TVP-09[(a)]. Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNNL quality assurance (QA) impact level II requirements.

A.1 Sampling Methodology

Standard glass tubes containing sorbent materials to trap vapors of selected analytes of NH_3, NO, NO_2, and H_2O (supplied by SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for vapor sampling. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration to perform workplace monitoring and because of available procedures and verification results associated with that particular application. The typical sorbent traps used consisted of a glass tube containing a sorbent material specific to the compound of interest. In general, the tubes contained two sorbent layers, or sections; the first layer was the primary trap, and the second layer provided an indication of breakthrough. In the tubes, sorbent layers are generally held in packed layers separated by glass wool. The sorbent traps, 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 NH_3 sorbent traps contained carbon beads impregnated with sulfuric acid; nominally, 500 mg were contained in the primary and 250 mg in the breakthrough sections. The NH_3 was chemisorbed as ammonium sulfate [$(NH_4)_2SO_4$]. The NO_2 traps contained a zeolite impregnated with triethanolamine (TEA), with 400 mg in the primary and 200 mg in the breakthrough sections. The NO_2 was absorbed and disproportionated to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). Glass tubes containing 800 mg of an oxidant such as chromate were used to convert NO to NO_2. The converted NO was then collected as nitrite and nitrate in an NO_2 trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sections.

(a) Pacific Northwest Laboratory. 12/95. *Sorbent Trap Preparation for Sampling and Analysis: Waste Tank Inorganic Vapor Samples*, PNL-TVP-09 (Rev. 2), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

Sorbent trains provided to trap inorganic compounds included all or some of the following: samples, spiked samples, spares, blanks, and spiked blanks. Sorbent trains were prepared from same-lot batches, with the oxidizer sections of the NO_x sorbent trains having been stored previously in a freezer. After sample preparation, sorbent trains were stored at $\leq$ 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_v) of a 3.00-L sample containing 75.0 μg of NH_3 equals

$$C_v = \frac{75.0\ \mu g}{17.0\ g/mol}\left[\frac{3.00\ L}{22.4\ L/mol}\right]^{-1} = 32.9\ ppmv \qquad (A.1)$$

This calculational method produces concentration results that are slightly conservative (greater than actual) because the volume of water vapor in the sample stream is neglected. The volume of water vapor is not included in the measured sampled volume because of its removal in desiccant traps upstream of the mass flowmeter. However, the bias is generally expected to be small. For a tank headspace temperature of 35°C, the magnitude of the bias would be about 1 to 6%, assuming tank headspace relative humidities of 20 to 100%, respectively. The concentration of mass (determined gravimetrically) was also per dry-gas volume at standard conditions.

A.2 Analytical Procedures

The compounds of interest were trapped using solid sorbents and chemisorption (adsorption of water vapor). Analytical results were based on extraction and analysis of selected ions. Analytical procedures used are specified in the text.

A.2.1 Ammonia Analysis. The sorbent material from the NH_3-selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-, or primary-, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the NH_3 sorbent traps were analyzed using the selective ion electrode procedure PNL-ALO-226 Rev. 0[(a)]. Briefly, this method includes 1) preparing a 1000-μg/mL (ppm) NH_3 stock standard solution from dried reagent-grade NH_4Cl and DIW, 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm NH_3 working calibration standards by serial dilution of the freshly made stock standard, 3) generating an initial calibration curve from the measured electromotive force signal versus NH_3 concentration data obtained for the set of working standards, 4) performing a calibration-verification check, using a mid-range dilution of a certified National Institute for Standards and Technology (NIST)-traceable 0.1 M NH_4Cl standard from an independent source, after analyzing every five or six samples, 5) continuing this sequence until all samples of the batch have been measured, including duplicates and spiked samples, and 6) remeasuring the complete set of calibration standards (at the end of the session). Electromotive force (volts) signal measurements obtained for samples are compared to those for standards, either graphically or algebraically (using linear regression) to determine NH_3 concentration in the samples.

A.2.2 Nitrite Analysis. The sorbent traps for NO_2 and NO were desorbed in an aqueous TEA and n-butanol solution and analyzed by suppressed-conductivity ion chromatography (SCIC) for nitrite according to PNL-ALO-212, Rev. 1[(b)] modified to obviate interferences by concentrations of non-target analytes. Specifically, the modifications used were 1) eluent 1.44 mM Na_2CO_3 + 1.8 mM $NaHCO_3$ at 2.0 mL/min, 2) one guard column (AG4A) and two separator columns (AS4A) in series instead of just one separator column, and 3) all standards, samples, and blanks were injected into the IC sample loop through 0.45-μm syringe filters.

For the analysis, the sorbent materials were placed into labeled 20-mL glass scintillation vials. To each vial, 3.0 mL of desorbing solution (15 g TEA + 1 mL n-butanol in 1.0 L of DIW) was added. Primary sorbent-tube sample materials and back-up (breakthrough) sorbent-trap materials were analyzed separately using identical procedures. Each analytical session was conducted as follows. Working nitrite standards (0, 0.1, 0.25, and 0.5 ppm) were prepared by diluting a stock nitrite standard with desorbing solution. An initial calibration curve was prepared from the instrument response (chromatographic peak height) versus nitrite standard concentration data for the set of working standards. A calibration verification check using one of the midrange standards was

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

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

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

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

A.2.3 Mass (Water) Analysis. Sorbent traps used to make each sample train were weighed using a semi-micro mass balance, after labeling and breaking the glass tube ends, without plastic end caps in accordance with procedure PNL-TVP-09. After receipt of exposed samples, the sorbent traps were again weighed to determine the change in mass. Records of the measurements were documented on sample-preparation data sheets. The mass concentration, generally roughly equal to the concentration of water, was determined by dividing the combined change in mass from all traps in a sorbent train by the actual volume of gas sampled. Field blanks were used to correct data.

A.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNNL documents including PNL-MA-70 (Part 3), PNL-ALO-212, PNL-ALO-226, and Quality Assurance Plan ETD-002. The samples were analyzed following PNNL Impact Level II. A summary of the analysis procedures and limits for the target inorganic compounds is provided in Table A.1. The table also shows generic expected notification ranges and describes related target analytical precision and accuracy levels for each analyte; the information in the table is based on the data quality objective assessment by Osborne et al. (1995). From the table, it can be seen that the EQL required to resolve the analyte at one-tenth of the recommended exposure limit for each of the target analytes is achieved using current procedures and with a vapor-sample volume of 3 L and a desorption-solution volume of 3 mL (10 mL for NH_3).

The accuracy of concentration measurements depends on potential errors associated with both sampling and analysis (see Section A.4). Sampling information, including sample volumes, was provided by WHC; sample-volume uncertainty was not provided. The uncertainty of analytical results, which depends on the method used, was estimated to be within allowable tolerances (Osborne et al. 1995; Table A.1). For NH_3 analyses, the accuracy of laboratory measurements by selective ion electrode was estimated to be $\pm$ 5% relative, independent of concentration at 1 μg/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 NO_2 and NO) are performed using certified but not NIST-traceable SRM; this is because NIST does not make a nitrite SRM. Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for NH_3 above, the estimated maximum bias for samples derived from sampling for NO_2 is $\pm$ 10%, and for samples derived from sampling for NO it is $\pm$ 5% relative.

Table A.1. Analytical Procedures, Quantification Limits, and Notification Levels for Selected Inorganic Analytes[a]

Analyte	Formula	Procedure	EQL[b] (μg)	EQL[b] (ppmv)	Notification Level[c] (ppmv)
Ammonia	NH_3	PNL-ALO-226	1.0	0.71	≥ 150
Nitrogen Dioxide	NO_2	PNL-ALO-212	0.3	0.16	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.3	0.16	≥ 50
Mass (water)[d]	n/a	PNL-TVP-09	0.6 mg	0.3 mg/L	n/a

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

A.4 Inorganic Sample Results

Samples were obtained by WHC from the tank headspace of Tank C-202 on June 25, 1996 using the ISVS. The sample job designation number was S6066. Samples were prepared, submitted to WHC for the sample job, and then returned to PNNL and analyzed to provide information on the concentrations of NH_3, NO_2, NO, and mass (primarily H_2O). Samples were controlled using COC form 100246 (Appendix D). The inorganic samples and sample volume information were received from WHC on July 10, 1996. Analyses were completed on July 16, 1996 (gravimetric, 21 days elapsed), July 22, 1996 (ammonia, 27 days elapsed), and July 18, 1996 (nitrite, 23 days elapsed).

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table A.2. The types of sample trains used and the order of sorbent traps within each train are also shown in the table. For example, the sorbent train $NH_3/NO_x/H_2O$ contained an NH_3 trap at the inlet end, a NO_x series in the middle (Section A.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table A.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank headspace concentration results (Table A.3) are based on this information, and the listed uncertainties equal plus or minus one standard deviation of the individual results from each set of samples. Percentage relative standard deviation (RSD) may be determined by dividing the standard deviation by the average result and multiplying by 100. Where analytical results from samples, corrected for blanks, were less than the EQL in Table A.1, the concentration results (Table A.3) are listed as "less-than" the EQL value. Results of control samples,

such as trip blanks, field blanks, and spiked blanks, are discussed in this section. Spiked blanks, when used, were transported to the field but not opened. Spiked samples, when used, were opened in the field and used to collect tank vapors. Sample results were not corrected for the percentage recoveries of spiked blanks.

A.4.1 Ammonia Results. The concentration of NH_3 was <0.7 ppmv, based on all four samples. Blank corrections, 0.09 μmol in front and 0.07 μmol in back sections, were about 67% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of $\pm$ 6.2%. One blank sorbent trap was spiked with 17 μt/mL of NH_3 and yielded a percentage recovery of 102%. One sample leachate was spiked after initial analysis with roughly the quantity of ammonia in the sample and yielded a percentage recovery of 90%. The initial and continuing calibration verification standards, using NIST-traceable material, yielded percentage recoveries of 97% (ICV) and 101% (CCV) during the analytical session. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 μg/mL.

A.4.2 Nitrogen Oxides Results. The concentrations of NO_2 and NO were both < 0.16 ppmv based on all four samples. Blank-corrected NO_2^- quantities in the sorbent traps were all < 0.013 μmol. Nitrite blank levels used to correct data were 0.0062 μmol in front (four of four blanks analyzed) and 0.0046 μmol in back (two of four blanks analyzed) sorbent sections. The analyses of two samples were duplicated and yielded repeatabilities of $\pm$ 0% and $\pm$ 2.0%. Two sample leachates were spiked with 0.25 and 0.125 ppm NO_2^- and yielded percentage recoveries of 97 and 99%. A 4-point calibration was performed over a concentration range of 0 to 0.5 μg NO_2^- per mL in the desorbing matrix. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 μmol NO_2^- during previous sample jobs yielded percentage recoveries of 153 $\pm$ 14, 103 $\pm$ 4, 106 $\pm$ 8, and 111 $\pm$ 7%, respectively (Clauss et al. 1994; Ligotke et al. 1994).

A.4.3 Gravimetric Results. Gravimetric results yield water vapor concentrations. This is because the total mass concentration of other vapors in the headspaces of Hanford waste tanks, measured in μg/L, are typically two or three orders of magnitude less than the mg/L mass concentrations of the water vapor found in even relatively dry tanks. The water vapor mass concentration collected in the 5-trap sorbent trains was 7.9 $\pm$ 0.3 mg/L, based on dry air sample volumes (0°C and 760 torr). The result was determined from an average mass gain of 19.0 mg from all four sample trains. The blank correction applied to the results was - 4.25 mg per train, based on a mass gain of 4.25 $\pm$ 0.21 mg per two 5-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of $\pm$ 0.1 mg. Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg water was 103 $\pm$ 2% during a previous sample job (Clauss et al. 1994).

Corrected for a measured tank headspace temperature of 19.6°C and pressure of 736.6 torr, the actual water vapor mass concentration from the gravimetric results was 7.1 $\pm$ 0.2 mg/L. Also based on analytical results, the partial pressure of water vapor was 7.2 $\pm$ 0.2 torr, the relative humidity was 42 $\pm$ 1%, and the dew point was 6.4 $\pm$ 0.2°C.

Table A.2 List of PNNL Inorganic Samples, Controls, and Gravimetric Results Obtained from the Headspace of Tank C-202 on 6/25/96

		Sample Port and Volume Information[a]				
Sample Number	Sorbent Train Type	Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
Samples:						
S6066-A07-16R	NH3/NOx/H2O	1	200.0	10.0	1.86	0.0189
S6066-A08-17R	NH3/NOx/H2O	2	200.0	10.0	1.86	0.0184
S6066-A09-18R	NH3/NOx/H2O	3	200.0	10.0	1.86	0.0196
S6066-A10-19R	NH3/H2O/H2O	4	200.0	10.0	1.86	0.0191
Controls:						
S6066-A15-20R	NH3/NOx/H2O Field Blank	n/a[b]	n/a	n/a	n/a	0.0041
S6066-A16-21R	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	0.0044

(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 the Headspace of Tank C-202 on 6/25/96

Sample	Analytical Results (μmol) Front Section	Back Section	Total[b] Blank-Corrected	Sample Volume (L)	Vapor[a] Concentration (ppmv)
NH_3 Samples:			<0.06	1.86	<0.71
S6066-A07-16R	0.11	0.045	<0.06	1.86	<0.71
S6066-A08-17R	0.14	NA[c]	<0.06	1.86	<0.71
S6066-A09-18R	0.14	0.062	<0.06	1.86	<0.71
S6066-A10-19R	0.14	NA	<0.06	1.86	<0.71
NO_2 Samples:			<0.013	1.86	<0.16
S6066-A07-16R	0.0068	NA	<0.013	1.86	<0.16
S6066-A08-17R	0.0069	0.0044	<0.013	1.86	<0.16
S6066-A09-18R	0.0062	NA	<0.013	1.86	<0.16
S6066-A10-19R	0.0062	0.0062	<0.013	1.86	<0.16
NO Samples:			<0.013	1.86	<0.16
S6066-A07-16R	0.0104	0.0037	<0.013	1.86	<0.16
S6066-A08-17R	0.0088	NA	<0.013	1.86	<0.16
S6066-A09-18R	0.0086	0.0054	<0.013	1.86	<0.16
S6066-A10-19R	0.0083	NA	<0.013	1.86	<0.16
Gravimetric Samples:			14.8 mg	1.86	7.9 ± 0.3 mg/L
S6066-A07-16R	n/a[c]	n/a	14.7	1.86	7.9
S6066-A08-17R	n/a	n/a	14.2	1.86	7.6
S6066-A09-18R	n/a	n/a	15.4	1.86	8.3
S6066-A10-19R	n/a	n/a	14.9	1.86	8.0

(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 ± 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_2 and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The level of analytes found in blanks is described in the subsections of Section A.4.

(c) NA = not analyzed; n/a = not applicable.

A.5 References

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

Ligotke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94 - 5/25/94).* PNL-10172, Pacific Northwest Laboratory, Richland, Washington.

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

Appendix B

Tank Vapor Characterization:

Permanent Gases

Appendix B

Tank Vapor Characterization: Permanent Gases

B.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant-free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02[(a)]. The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis. 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.

B.2 Analytical Procedure

The SUMMA™ canister samples were analyzed for permanent gases according to PNNL Technical Procedure PNL-TVP-05[(b)] with the exceptions listed in the following text and in the quality assurance/quality control section of this report. This method was developed in-house to analyze permanent gases, defined as hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and nitrous oxide (N_2O), by gas chromatograph/thermal conductivity detection (GC/TCD). Aliquots of sampled air are drawn directly from each canister into a 5-mL gas-tight syringe and injected into a Hewlett-Packard 5890 GC/TCD fitted with a loop injector valve and a column switching valve. An aliquot of 5 mL is used so that the 1.0-mL injection loop is completely purged with sample air, ensuring that no dilution of the sample takes place within the injection loop. One set of GC conditions is used to analyze for CO, CO_2, N_2O, and CH_4 using Helium (He) as the carrier gas. A second GC analysis is performed for H_2 (using nitrogen as the carrier gas) to enhance the signal sensitivity and lower the detection limit for this analyte. The permanent gases and associated EQLs are listed in Table B.1.

(a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

(b) Pacific Northwest Laboratory. 5/96. *Analysis Method for the Determination of Permanent Gases in Hanford Waste Tank Vapor Samples Collected in SUMMA™ Passivated Stainless Steel Canisters*, PNL-TVP-05 (Rev. 2). PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

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

Analyte	Formula	Procedure	Estimated Quantitation Limit (ppmv)
Carbon Dioxide	CO_2	PNL-TVP-05	17
Carbon Monoxide	CO	PNL-TVP-05	17
Methane	CH_4	PNL-TVP-05	25
Hydrogen	H_2	PNL-TVP-05	17
Nitrous Oxide	N_2O	PNL-TVP-05	17

B.3 Quality Assurance/Quality Control

Standards for the permanent gas analysis were blended from commercially prepared and certified standards for each of the analytes reported in Table B.1. The instrument was calibrated for CH_4 over a range of 25 to 2100 parts per million by volume (ppmv) and for CO, CO_2, and N_2O over a range of 17 to 2100 ppmv using standards at five different concentrations and He as a carrier gas. A similar procedure was followed for H_2 with a range of 17 to 2120 ppmv, except the carrier gas was changed to N_2. An average response factor from the calculation was used for quantification of compound peak area.

Each analyte was quantitated by comparison of sample analyte peak area to the calibration plot generated for the compound. The estimated quantitation limit (EQL) for the method has been established as the low level calibration standard. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within $\pm$ 25% of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N_2 reagent blank, an ambient-air sample collected $\sim$10 m upwind of Tank C-202, and the ambient air collected through the In Situ Vapor Sampling System (ISVS) 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 August 12, 1996 under COC WHC 100244 (see Appendix D). The samples were analyzed on September 15, 1996.

SUMMA™ canisters for Tank C-202 were received from WHC with radiation concerns. In order to demonstrate that the tank samples did not exceed radiation limit criteria, SUMMA™ canister PNL 128 was attached to SUMMA™ canister PNL 011. The contents of PNL 128 were allowed to equilibrate through a filter and into PNL 011. The filter was measured and the results verified that the SUMMA™ canisters were below the radiation limit criteria. The SUMMA™ canister samples were released to the VAL on September 13, 1996. Both SUMMA™ canisters were analyzed for all permanent gases. The pressures of both SUMMA™ canisters were less than 400 torr, but the low

pressures presented no problem for introducing 1 mL of sample at STP into the analytical system. The analytical results from SUMMA™ canister PNL 128 were reported, and these results were not significantly different from those of SUMMA™ canister PNL 011.

Table B.2 lists results of the permanent gas analysis from samples collected from the headspace of Tank C-202, ambient air collected ~10 m upwind of the tank, and ambient air collected through the ISVS. Carbon dioxide at 402 ppmv was the only permanent gas observed above the method EQL in the tank headspace samples. A duplicate analysis was performed on SUMMA™ canister PNL 129; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

Table B.1 Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank C-202 and for Ambient Air and Ambient Air Through the ISVS Collected near Tank C-202 in SUMMA (TM) Canisters on 6/25/96

Permanent Gas Analyte	Ambient Air Upwind S6066-A01.123[a] PNL 123[b] Concentration (ppmv)	Ambient Air Through Bundle S6066-A02.127[a] PNL 127[b] Concentration (ppmv)	Tank Samples S6066-A04.128[a] PNL 128[b] Concentration (ppmv)	Tank Samples S6066-A05.129[a] PNL 129[b] Concentration (ppmv)	Tank Samples S6066-A06.134[a] PNL134 [b] Concentration (ppmv)	Tank Samples S6066-A05.129[a] PNL 129 [b][c] Concentration (ppmv)	Average Concentration Tank Samples (ppmv)
Hydrogen	<17	<17	<17	<17	<17	<17	<17
Methane	<25	<25	<25	<25	<25	<25	<25
Carbon Dioxide	379	385	400	404	403	406	402
Carbon Monoxide	<17	<17	<17	<17	<17	<17	<17
Nitrous Oxide	<17	<17	<17	<17	<17	<17	<17

(a) WHC sample identification number.
(b) PNL canister number.
(c) Replicate analysis for PNL 129; results are not included in the calculation of average concentrations.

Appendix C

Tank Vapor Characterization:

Total Non-Methane Organic Compounds

Appendix C

Tank Vapor Characterization: Total Non-Methane Organic Compounds

C.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant-free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02[(a)]. The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis. 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[(b)], which is similar to U.S. Environmental Protection Agency (EPA) compendium Method TO-12. The method detection limits in the sub mg/m^3 are required to determine total non-methane organic compounds (TNMOC) concentration in the tank samples.

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

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

(a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

(b) Pacific Northwest Laboratory. 12/95. *Determination of TO-12 Total Nonmethane Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Flame Ionization Detection*, PNL-TVP-08 (Rev. 1), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

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

C.3 Quality Assurance/Quality Control

This method requires user calibration (category 2 measuring and test equipment) of the analytical system in accordance with QA plan ETD-002.

The TNMOC is calibrated by using propane as the calibration standard. The instrument calibration mixture for the PNL-TVP-08 analysis consists of National Institute for Standards and Technology (NIST) 99.999% propane analyzed using a five-point, multi-level, linear regression curve.

A continuing calibration verification (CCV) standard of 100 ppmv propane is analyzed to confirm acceptability of instrument performance. The initial calibration is then used to quantify the samples.

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

Before the tank samples were analyzed, a diagnostic check was performed on the GC/FID instrument by running a system cleanliness procedure and an instrument continuing calibration as described in PNL-TVP-08. First, two blank volumes of Aadco purified air were analyzed to check the cleanliness of the system. This demonstrates through the analysis of a zero-air blank that the level of interference is acceptable in the analytical system. The system should be cleaned to 0.1 mg/m^3 of TNMOCs. Second, an instrument continuing calibration is run using 100-mL UHP propane analyzed using the response factor as an external standard method followed by one blank volume of Aadco air.

C.3.1 Quantitation Results of Target Analytes. The mg/m^3 was derived from the five-point multilevel calibration curve from the propane standard using the following equation:

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

The ng/m^3 concentrations are calculated from mg/m^3 using the equation:

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

C.4 Total Non-Methane Organic Compounds Sample Results

Five SUMMA™ canisters were returned to the laboratory on August 12, 1996 under WHC COC 100244 (see Appendix D). The samples were analyzed on September 17, 1996.

SUMMA™ canisters for Tank C-202 were received from WHC with radiation concerns. In order to demonstrate that the tank samples did not exceed radiation limit criteria, SUMMA™ canister PNL 128 was attached to SUMMA™ canister PNL 011. The contents of PNL 128 were allowed to equilibrate through a filter and into PNL 011. The filter was measured and the results verified that the SUMMA™ canisters were below the radiation limit criteria. The SUMMA™ canister samples were radiologically released to the VAL on September 13, 1996. Both SUMMA™ canisters were diluted to twice the resulting atmospheric pressure, less than 800 torr, but the low pressures presented no problem for introducing 100 mL of sample into the TO-12 analytical system. The analytical results from SUMMA™ canister PNL 128 were reported, and these results were not significantly different from those of SUMMA™ canister PNL 011.

Table C.1. lists results of the TO-12 gas analysis from samples collected from the headspace of Tank C-202, ambient air collected ~10 m upwind of the tank, and ambient air collected through the vapor sampling system. The concentrations in both ambient air samples were < 0.59 mg/m^3. Concentrations in the three tank headspace samples ranged from 1.04 mg/m^3 to 1.35 mg/m^3, with an average concentration of 1.23 mg/m^3. A replicate analysis was performed on SUMMA™ canister PNL 129; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

A deviation was made to the current procedure (PNL-TVP-08) and documented in Vapor Deviation Report #JAE082996. The following is a discussion of the deviation:

> 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 always present, the average response factor method generates a large apparent nonlinearity introducing an unnecessary amount of level dependent error. To correct this situation, data included in this and all subsequent calibrations shall use a linear regression fit which includes both a slope and intercept. The correlation coefficient for this ten point calibration curve is 0.99996, an extremely well ordered data set. The low level standard is used as the EQL in accordance with Vapor Deviation Report #KLS102496. Sample results are flagged with a "less-than" symbol (<) when less than the EQL value. A new revision to procedure PNNL-TVP-08 currently under preparation will reflect these amendments.

The reported concentration of 1.23 mg/m^3 was below the cutoff value of 5.0 mg/m^3 set forth by WHC. TO-12 tank sample results below the cutoff value were not analyzed for organic species. Therefore, no further analysis was conducted on the tank headspace samples from Tank C-202.

Table C.1 TO-12 Results for Samples Collected Through the ISVS from the Headspace of Tank C-202 and from Ambient Air Near Tank C-202 in SUMMA (TM) Canisters on 6/25/96.

	Ambient Air Upwind S6066-A01.123[a] PNL 123[b] Concentration (mg/m3)	Ambient Air Through Bundle S6066-A02.127[a] PNL 127[b] Concentration (mg/m3)	Tank Samples					
			S6066-A04.128[a] PNL 128[b] Concentration (mg/m3)	S6066-A05.129[a] PNL 129[b] Concentration (mg/m3)	S6066-A06.134[a] PNL 134[b] Concentration (mg/m3)	S6066-A04.011[a] PNL 011[b][d] Concentration (mg/m3)	S6066-A05.129[a] PNL 129[b][c] Concentration (mg/m3)	Average Concentratio Tank Sample (mg/m3)
TO-12	<0.59	<0.59	1.04	1.30	1.35	1.17	1.34	1.23

(a) WHC sample identification number.
(b) PNL canister number.
(c) Replicate analysis for PNL 129; results are not included in the calculation of average concentrations.
(d) Contents of PNL 128 transfered into PNL 011 for radiation screening prior to analysis; results are not included in the calculation of average concentrations.

Appendix D

Tank Vapor Characterization:

Chain of Custody Sample Control Forms

Battelle Pacific National Northwest Lab	CHAIN OF CUSTODY	WHC 100246

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) 373-7437
Page 85-9656 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm
241-C-202 Tank Vapor Sample SAF S6066
(ISVS Cart)

Collection date 06 - 25 - 96
Preparation date 06 - 17 - 96

Ice Chest No.

Field Logbook No. WHC-N-697-8

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

S6066 - A07 . 16R	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6066 - A08 . 17R	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6066 - A09 . 18R	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6066 - A10 . 19R	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6066 - A15 . 20R	Open, close and store $NH_3/NO_x/H_2O$ field blank #1
S6066 - A16 . 21R	Open, close and store $NH_3/NO_x/H_2O$ field blank #2

[ ] Field Transfer of Custody [X] Chain of Possession (Sign and Print Names)

Relinquished By	Date	Time	Received By	Date	Time
G W Dennis G. W. Dennis	06 - 20 -96	1150	J A Edwards J A Edwards	06 - 20 -96	1150
6-24-96 ~~J A Edwards~~ J L Tulya Janet L Tulya	06 -24-96	1327	G S CAPRIO G S Caprio	06 -27-96	1327
G S CAPRIO G S Caprio	07-10-96	1435	J A EDWARDS J A Edwards	7-10-96	1435
J A Edwards J A Edwards	7-11-96	1400	G.W. Dennis G. W. Dennis	7-11-96	1400
G.W. Dennis G.W. Dennis	7-17-96	1245	K.H. Pool J Carl Pool	7-17-96	1245

Final Sample Disposition

Comments:

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

POC [signature] POC [signature]

(WHC-SD-WM-TP-335, REV. 2, Table 2b)
A-6000-407 (12/92) WEF061

1 of 1

(Revised 05/30/96 PNNL)

Battelle Pacific National Northwest Lab	CHAIN OF CUSTODY	WHC 100244

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-C-202 Tank Vapor Sample SAF S6066 (ISVS Cart) — Collection date 06 - 25 - 96, Preparation date 06 - 23 - 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

S6066 - A01 . 123	Collect Ambient Air Sample SUMMA #1
S6066 - A02 . 127	Collect Ambient Air Sample SUMMA #2 (through tube bundle)
S6066 - A04 . 128	Collect SUMMA #3-A / S6066-A04.011 SUMMA #3-B
S6066 - A05 . 129	Collect SUMMA #4
S6066 - A06 . 134	Collect SUMMA #5

[ ] Field Transfer of Custody [X] Chain of Possession (Sign and Print Names)

Relinquished By	Date	Time	Received By	Date	Time
J L Julya [signature]	06-24-96	1321	GS CAPRIO [signature]	06-24-96	1327
GS CAPRIO / [signature]	08-12-96	1530	HA EDWARDS [signature]	08-12-96	1530

Final Sample Disposition

Comments:
TRANSFER OF SUMMA #3 / A04.128 INTO A04.011 ON 09-12-96 / RAD RELEASED 09/13/96

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

POC [signature] POC [signature]

(WHC-SD-WM-TP-335, REV. 2, Table 2b) (Revised 05/30/96 PNNL)

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PNNL

Karl Pool	P8-08
Berta Thomas	P8-08
John Evans	K6-96
Khris Olsen	K6-96
Kurt Silvers	K9-08
Jon Fruchter	K6-96
Jim Huckaby	K6-80
Brenda Thornton	K6-80
Darlene Varley	K1-06
Katherine Savard	K9-04
Kris Walters	K6-80 (5 copies)

Lockheed

Larry Pennington	S7-21
Luther Buckley	R2-12

DOE-RL

Carol Babel	S7-54
Jim Thompson	S7-54