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# Vapor Space Characterization of Waste Tank 241-TY-104 (*In Situ*): Results from Samples Collected on 8/5/94

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# DISCLAIMER

# Summary

This report describes inorganic and organic analyses results from *in situ* samples obtained from the headspace of the Hanford waste storage Tank 241-TY-104 (referred to as Tank TY-104). The results described here were obtained to support safety and toxicological evaluations. A summary of the results for inorganic and organic analytes is listed in Table 1. Detailed descriptions of the results appear in the text.

Quantitative results were obtained for the inorganic compounds ammonia ($NH_3$), nitrogen dioxide ($NO_2$), nitric oxide (NO), and water ($H_2O$). Sampling for hydrogen cyanide (HCN) and sulfur oxides ($SO_X$) was not performed. In addition, we looked for the 39 TO-14 compounds plus an additional 14 analytes. Of these, eight were observed above the 5-ppbv reporting cutoff. Twenty-four organic tentatively identified compounds (TICs) were observed above the reporting cutoff of (ca.) 10 ppbv and are reported with concentrations that are semiquantitative estimates based on internal-standard response factors. The 10 organic analytes with the highest estimated concentrations are listed in Table 1 and account for approximately 86% of the total organic components in Tank TY-104.

**Table 1.** Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank TY-104 on 8/5/94

| Category | Analyte | Vapor[(a)] Concentration | Units |
|---|---|---|---|
| Inorganic | $NH_3$ | 50 ± 1 | ppmv |
| | $NO_2$ | $\leq$ 0.02 | ppmv |
| | NO | 0.13 ± 0.01 | ppmv |
| | $H_2O$ | 20 ± 10 | mg/L |
| Organic | 3-Methylhexane | 4.68 | $mg/m^3$ |
| | 2-Methylhexane | 2.85 | $mg/m^3$ |
| | 2,3-Dimethylpentane | 2.36 | $mg/m^3$ |
| | Acetone | 2.24 | $mg/m^3$ |
| | Methylcyclohexane | 1.15 | $mg/m^3$ |
| | 3,3-Dimethylpentane | 1.04 | $mg/m^3$ |
| | 3-Ethylpentane | 0.97 | $mg/m^3$ |
| | Heptane | 0.64 | $mg/m^3$ |
| | 1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON-113) | 0.46 | $mg/m^3$ |
| | Trichlorofluoromethane (FREON-11) | 0.42 | $mg/m^3$ |

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

# Acknowledgments

The authors gratefully acknowledge the support of other project staff at Pacific Northwest Laboratory who contributed to the successful completion of this sampling and analysis activity. Jeff Edwards served as the PNL single-point-of-contact and coordinated sample handling and communications with Westinghouse Hanford Company. K. B. Olsen assisted in preparing the organic portion of this report. Sally Slate, May-Lin Thomas, and Karen Schielke analyzed inorganic samples, and Gary Dennis prepared the solid-sorbent sample trains. Bonnie L. Lehrman provided word processing support.

# Abbreviations

| | |
|---|---|
| CAS | Chemical Abstracts Service |
| COC | chain of custody |
| $C_v$ | concentration by volume |
| DIW | deionized water |
| emf | electromotive force |
| EPA | U.S. Environmental Protection Agency |
| GC/MS | gas chromatography/mass spectrometry |
| HP | Hewlett Packard |
| IC | ion chromatography |
| IL | impact level |
| IS | internal standard |
| ISS | In-Situ-Sampling |
| MDL | minimum detection limit |
| NIST | National Institute for Standards and Technology |
| NPH | normal paraffin hydrocarbon |
| OSHA | Occupational Safety and Health Administration |
| PFA | perfluoroalkoxy |
| PNL | Pacific Northwest Laboratory |
| ppbv | part per billion by volume |
| ppmv | part per million by volume |
| QA | quality assurance |
| REL | recommended exposure limit |
| RPD | relative percent difference |
| SCIC | suppressed-conductivity ion chromatography |
| SIE | selective ion electrode |
| SRM | standard reference material |
| STP | standard temperature and pressure |
| TEA | triethanolamine |
| TIC | tentatively identified compound |
| VSS | vapor sampling system |
| WHC | Westinghouse Hanford Company |

# Contents

# Tables

# Figures

# 1.0 Introduction

This report describes results of the analyses of in-situ tank-headspace samples taken from the Hanford waste Tank 241-TY-104 (referred to as Tank TY-104). Pacific Northwest Laboratory (PNL)[a] contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and to analyze inorganic and organic analytes collected from the tank headspace and ambient air near the tank. The organic analytes for TO-14 compounds were extended to include 14 analytes identified by the Toxicological Review Panel for Tank C-103 and reported by Mahlum et al. (1994). Program management included these analytes for future tank analyses as identified in the fiscal year work plan. This plan is attached to a letter dated 9/30/94 and addressed to Mr. T. J. Kelly of WHC. The sample job was designated S4063, and samples were collected by WHC on August 5, 1994, using the *in situ* sampling system (ISS). While at WHC, inorganic samples for two jobs were swapped before either tank was sampled; consequently, although the sample job was S4063, the samples reported here are designated with identification numbers beginning with "S4061". The results of the analyses are expected to be used to estimate the potential toxicity of tank-headspace gas as described in *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution*, WHC-SD-WM-DQO-002, Rev. 0.

Sampling devices, including three sorbent trains (for inorganic analyses), and six SUMMA™ canisters (for organic analyses) were supplied to the WHC sampling staff on August 3 and 4. Samples were taken (by WHC) from the tank headspace on August 5 and were returned to PNL from the field on August 23. Inorganic (sorbent trap) samples actually used to sample TY-104 (see above note) were delivered to PNL on chain of custody (COC) 007490 (see Figure 1.1a). Upon receipt of the sampling information on 11/15/94, it was noted that the HCN samples had not been exposed by WHC to headspace vapors; analyses of those samples for $CN^-$ had already been accomplished by that date. Because of this, the $CN^-$ results were not reported. The SUMMA™ canisters were delivered on COC 007493 (see Figure 1.1b).

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 before implementation of PNL Technical Procedure PNL-TVP-07[b]. Custody of the sorbent traps was transferred to PNL personnel performing the inorganic analysis and stored at refrigerated (≤ 10°C) temperature until the time of analysis. The canister was stored in the 326/23B laboratory at ambient (25°C) temperature until the time of analysis. Access to the 326/23B laboratory is limited to PNL personnel working on the waste-tank safety program. Analyses described in this report were performed at PNL in the 300 area of the Hanford Reservation. Analytical methods that were used are described in the text. In summary, sorbent traps for inorganic analyses containing sample materials were either weighed (for water analysis) or weighed and desorbed with the appropriate aqueous solutions (for ammonia, nitrogen dioxide, and nitric oxide analyses). The aqueous extracts were analyzed by either selective electrode or ion chromatography (IC). Organic analyses were performed using cryogenic preconcentration followed by gas chromatography/mass spectrometry (GC/MS).

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[a] Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

[b] PNL-TVP-07, Rev. 0, October 1994, *Sample Shipping and Receiving Procedure for PNL Waste Tank Samples*, PNL-Technical Procedure, Tank Vapor Project, Richland, Washington.

| Westinghouse Hanford Company | CHAIN OF CUSTODY | WHC 007490 |
|---|---|---|

Custody Form Initiator J. A. Edwards — Telephone (509) 373-0141, Pager 85-3009

Company Contact L. A. Pingel — Telephone (509) 373-4051

Project Designation/Sampling Locations 200 East Tank Farm
241-TY-~~101~~ 104 Tank Vapor Sample SAF ~~S4061~~ S4063
Ice Chest No. 2Feb95 (IN-SITU) 2Feb95

Collection Date 08 - 05 - 94
Preparation Date 08 - 03 - 94
Field Logbook No. WHC-N-292-1 2Feb95

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to WHC

Possible Sample Hazards/Remarks Unknown at time of sampling

## Sample Identification

TY-104 (SA-063)

S4061 - ___ .34W NH3/NOx/H2O ~~(Sample #1)~~ RLM 2Feb95 (Spare)
S4061 - ___ .35W NH3/NOx/H2O ~~(Sample #2)~~ (Set 2, Port 1)
S4061 - ___ .36W NH3/NOx/H2O ~~(Sample #3)~~ (Set 2, Port 2)

S4061 - ___ .37W HCN/H2O ~~(Sample #1)~~ RLM 2Feb95 Spare
S4061 - ___ .38W HCN/H2O ~~(Sample #2)~~ Spare
S4061 - ___ .39W HCN/H2O ~~(Sample #3)~~ Spare

S4061 - ___ .40W OVS/Drier ~~(Radiological survey)~~ (Set 1, Port 1)

S4061 - ___ .41W NH3/NOx/H2O ~~(Spare)~~ RLM 2Feb95 (Set 2 Port 3)
S4061 - ___ .42W HCN/H2O (Spare) Spare

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

| Relinquished By | Date | Time | Received By | Date | Time |
|---|---|---|---|---|---|
| J. A. Edwards | 08-03-94 | 1530 | ~~S. M. Brown~~ Neil Buechler | 08-03-94 | 1530 |
| N. Buechler | 08-5-94 | 0800 | A. G. Krzan | 8-5-94 | 0800 |
| A. G. Krzan | 08/23/94 | 1415 | SM Brown | 8-23-94 | 1415 |
| SM Brown | 8/23/94 | 1415 | JAEdwards | 8-23-94 | 1915 |
|  |  |  |  |  |  |
|  |  |  |  |  |  |

(version 02-28-94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

Comments

A-6000-407 (12/92) WEF061

Figure 1.1a Chain-of-Custody for Inorganic Samples for Tank TY-104

| Westinghouse Hanford Company | CHAIN OF CUSTODY | WHC 007493 |
|---|---|---|

Custody Form Initiator J. A. Edwards
Telephone (509) 373-0141
Pager 85-3009

Company Contact L. A. Pingel
Telephone (509) 373-4051

Project Designation/Sampling Locations 200 East Tank Farm
241-TY-104 Tank Vapor Sample SAF S4063
(IN-SITU)
Ice Chest No.

Collection Date 08 - 0 5 - 94
Preparation Date 08 - 0 4 - 94
Field Logbook No.WHC-N-~~24~~2-1
2 Feb 95

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to WHC

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

| | |
|---|---|
| S4063 - ___ 164 | (PNL) SUMMA Ambient Air |
| S4063 - ___ 041 | (PNL) SUMMA Sample #1 |
| S4063 - ___ 063 | (PNL) SUMMA Sample #2 |
| S4063 - ___ 064 | (PNL) SUMMA Sample #3 |

| [X] Field Transfer of Custody | | | [ ] Chain of Possession | (Sign and Print Names) | |
|---|---|---|---|---|---|
| Relinquished By | Date | Time | Received By | Date | Time |
| J. A. Edwards J A Edwards | 08-04-94 | 1215 | N. Buechler N Buechler | 08-04-94 | 1215 |
| N Buechler N Buechler | 8-4-94 | 1245 | A. G. Rozzo | 8-5-94 | 0800 |
| A G Rozzo / [illegible] | 8-23-94 | 1415 | SM Brown / [illegible] | 8-23-94 | 1415 |
| SM Brown / [illegible] | 8-23-94 | 1415 | [illegible] / J A Edwards | 8-23-94 | 1415 |
| | | | | | |
| | | | | | |

(version 02-28-94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

Comments

A-6000-407 (12/92) WEF061

Figure 1.1b Chain-of-Custody for Organic Samples for Tank TY-104

# 2.0 Inorganic Task

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to WHC for sampling the tank headspace using the ISS. Controls and exposed samples were returned to PNL 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 VSS connected to the headspace of Tank C-103 (Ligotke et al. 1994). During those sample jobs, control samples provided validation that samples were effectively trapping $NH_3$ and mass. Sample preparation, handling, and disassembly were performed as described in Technical Procedure PNL-TVP-09[a]. Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNL quality assurance (QA) impact level (IL) III requirements.

## 2.1 Standard Sampling Methodology

Standard glass traps containing sorbent materials to trap vapors of selected analytes of $NH_3$, $NO_2$, NO, and $H_2O$ (SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for use by WHC. 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. 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 tubes, having glass-sealed ends, were received from the vendor. Sorbent traps were connected end-to-end to prepare multi-trap sorbent trains for sampling.

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.

Samples provided by PNL to trap inorganic compounds include all or some of the following: samples, spiked samples, spares, single trap blanks, and spiked blanks. The samples of each 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, all samples, spiked samples, blanks, and

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(a) Pacific Northwest Laboratory. 10/94. *Sorbent Trap Preparation for sampling and Analysis: Waste Tank Inorganic Vapor Samples*, PNL-TVP-09 (Rev.0), PNL Technical Procedure, Richland, Washington.

spiked blanks were stored at ≤ 10°C, primarily 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, and selected oxidizer sections were returned to a freezer until completion of analyses.

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 2.4. 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 (PFA)-grade Teflon® tubing. The tubing was heated in hot air and forced over the open ends of the traps to form a tight seal. Both the inlet and outlet ends of the sorbent trains (the downstream ends of the traps always contained silica gel) were each sealed with red-plastic end caps provided by the manufacturer. The leading and trailing ends of the sorbent trains remained sealed other than during the actual sampling periods. C-Flex® tubing was provided by WHC to connect the downstream ends of the sorbent trains to the sampling exhaust manifold connections.

**2.1.1 Concentration Calculations**. The concentrations of target compounds in the tank headspace were determined from sample results, assuming effective sample transport to the sorbent traps. Concentration, in parts per million by volume (ppmv), was determined by dividing the mass of the compound, in μmol, by the volume of the dried tank air sampled in mol. The micromolar sample mass was determined by dividing the compound mass, in μg, by the molecular weight of the compound, in g/mol. The molar sample volume was determined, excluding water vapor, by dividing the standard sample volume (at 21.1°C and 760 torr), in L, by 24.1 L/mol. For example, the concentration ($C_v$) of a 3.00-L sample containing 75.0 μg of $NH_3$ equals

$$C_v = \frac{75.0\ \mu g}{17\ g/mol}\left(\frac{3.00\ L}{24.1\ L/mol}\right)^{-1} = 35.4\ ppmv \qquad (2.1)$$

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.

## 2.2 Analytical Procedures

The compounds of interest were trapped using solid sorbents and chemisorption (adsorption of water vapor). Analytical results were based on extraction and analysis of selected ions. Analytical procedures used are specified in the text. All are compiled in PNL-MA-599.

**2.2.1 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 (SIE) procedure PNL-ALO-226[a]. Briefly, this method includes 1) preparing a 1000-$\mu$g/mL (ppm) $NH_3$ stock standard solution from dried reagent-grade $NH_4Cl$ and DIW on the day analyses are performed; 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 (emf) signal versus $NH_3$ concentration data obtained for the set of working standards; 4) performing a calibration-verification check, using one of the midrange standards, after analyzing every four or five samples; 5) continuing this sequence until all samples of the batch have been measured, including duplicates and spiked samples; and 6) remeasuring the complete set of calibration standards (at the end of the session). Emf signal measurements obtained for samples are compared to those for standards, either graphically or algebraically (using linear regression) to determine $NH_3$ concentration in the samples.

**2.2.2 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 injected into the IC sample loop through 0.45-$\mu$m syringe filters.

For the analysis, the sorbent materials were placed into labeled 20-mL glass scintillation vials. To each vial, 3.0 mL of desorbing solution (15 g TEA + 1 mL n-butanol in 1.0 L 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 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.

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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.

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

## 2.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNL documents. The samples were analyzed following PNL IL III. The PNL documents include PNL-MA-70 (Part 2), PNL-MA-599, PNL-ALO-212, PNL-ALO-226, and MCS-033. A summary of the analysis procedures and limits for the target inorganic compounds is provided in Table 2.1. From the table, it can be seen that the minimum detection limit (MDL) required to resolve the analyte at one-tenth of the recommended exposure limit (REL) 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 $NH_3$).

**Table 2.1** Analysis Procedures and Typical Detection Limits of Target Inorganic Analytes.

| Analyte | Formula | Procedure | REL[(a)] (ppmv) | 0.1 x REL[(a)] (ppmv) | MDL[(b)] (ppmv) |
|---|---|---|---|---|---|
| Ammonia | $NH_3$ | PNL-ALO-226 | 25 | 2.5 | 0.5 |
| Nitrogen Dioxide | $NO_2$ | PNL-ALO-212 | 1 | 0.1 | 0.02 |
| Nitric oxide | NO | PNL-ALO-212 | 25 | 2.5 | 0.02 |
| Mass (water)[(c)] | n/a | n/a | n/a | n/a | n/a |

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(a) Target analytical limits are equal to one-tenth of the REL.

(b) MDL is defined as the vapor concentration that can be detected with an uncertainty equal to about the magnitude of the measurement. The uncertainty is expected to reduce to about one-quarter of the magnitude of the measurement at a concentration of four times the MDL. The MDLs were based on the assumption that 3 L of vapor are sampled; if greater volumes of vapor are sampled, correspondingly smaller MDLs can be achieved. The MDLs were also based on desorbing-solution volumes of 10 mL for $NH_3$ and 3 mL for the other analytes.

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

The accuracy of concentration measurements depends on errors associated with both sampling and analysis (see Section 2.4). Sampling information, including sample volumes, was provided by WHC; sample volume uncertainty was not provided. The accuracy of analytical results depends on the method used. For $NH_3$ analyses, the accuracy of laboratory measurements by SIE was estimated to be ± 5% relative, independent of concentration at 1 $\mu$g/mL or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Unfortunately, no known National Institute for Standards and Technology (NIST)-traceable standard reference material (SRM) is available against which to compare working standards. Similarly, no known NIST SRM is available for nitrite analysis (for $NO_2$ and NO). Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for $NH_3$ above, the estimated maximum bias in the laboratory analysis of samples derived from sampling for $NO_2$ is ± 10%, and for samples derived from sampling for NO, it is ± 5% relative.

The accuracy of measurements of sample mass is ± 0.05 mg, or much less than 1% of the mass changes of most samples, and roughly 10% or less of the mass change of most blanks. The analytical accuracy of measurements of the change in mass of sorbent trains is estimated to be ± 1 mg per 5-trap sorbent train; this estimate is based largely on preliminary information that unopened field-blank sorbent trains gain 0.3 ± 0.4 mg per train.

## 2.4 Inorganic Sample Results

Sorbent trap trains and controls were prepared on 8/2/94, submitted to WHC on 8/3/94, and used by WHC to sample the tank headspace of Tank TY-104 on 8/5/94 using the ISS. The sample job designation number was S4063. The exposed samples were returned to PNL on 8/23/94 and subsequently analyzed on 8/25/94 ($H_2O$), 9/9/94 ($NH_3$), and 9/15/94 ($NO_x$) to provide information on the vapor-space concentrations of selected inorganic compounds. Sampling for HCN and sulfur oxides was not performed by WHC. (Samples for HCN were provided but not used to sample the headspace.) The sample volume information was received from WHC on 11/15/94.

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table 2.2. 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, an $NO_x$ series in the middle (Section 2.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table 2.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank-headspace concentration results (Table 2.3) 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. Where analytical results from samples were nearly indistinguishable from those of blanks, indicating very low vapor concentrations of the analyte, the concentration results (Table 2.3) are listed as "less than or equal to" a probable maximum value determined by subtracting the average of the blanks less one standard deviation from the average of the samples plus one standard deviation. Results of control samples, such as 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.

**2.4.1 Ammonia Results**. The concentration of $NH_3$ was 50 ± 1 ppmv, based on all three samples. The blank-corrected $NH_3$ quantities in the sorbent traps ranged from 8.7 to 9.2 $\mu$mol in the front sorbent sections; back sections were not analyzed. Blank corrections, $\leq 0.06$ $\mu$mol in front sections and $\leq 0.03$ $\mu$mol in back sorbent sections, were less than 1% of collected quantities and were neglected. Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 $\mu$mol of $NH_3$ were 101 ± 4%, 109 ± 2%, and 104 ± 1%, respectively, during related sample jobs (Clauss et al. 1994; Ligotke et al. 1994). The analysis of one sample was duplicated and yielded a repeatability of ± 4%. One sample leachate was spiked after

**Table 2.2** List of PNL Inorganic Samples, Controls, and Gravimetric Results Obtained From *In Situ* sampling of Headspace of Tank TY-104 on 8/5/94

| | | Sample Port and Volume Information[a] | | | |
|---|---|---|---|---|---|
| Sample Number | Sorbent Type | Flow Rate (mL/min) | Duration (min) | Volume (L) | Mass Gain (g) |
| Samples: | | | | | |
| S4063- 061-35W | $NH_3/NO_x/H_2O$ Train | 287 | 15.0 | 4.30 | 0.1340 |
| S4063- 061-36W | $NH_3/NO_x/H_2O$ Train | 288 | 15.0 | 4.32 | 0.0769 |
| S4063- 061-41W | $NH_3/NO_x/H_2O$ Train | 290 | 15.0 | 4.35 | 0.0581 |
| S4063- 061-34W | $NH_3/NO_x/H_2O$ Blank/Spare | n/a[b] | n/a | n/a | 0.0024 |

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(a) Sampling information and dry-gas sample volumes, corrected to 21°C and 760 torr, were provided by WHC. Uncertainty values were not provided with sample-volume results.

(b) n/a = not applicable.

initial analysis with roughly the quantity of $NH_3$ in the sample and yielded a percentage recovery of 101%. A 5-point calibration was performed over an $NH_3$ range of 0.1 to 1000 $\mu$g/mL.

**2.4.2 Nitrogen Oxides Results**. Measurements of $NO_2$ and NO were made using three 5-segment $NH_3/NO_x/H_2O$ sorbent-trap trains (the $NO_x$ trains consisted of $NO_2$ trap, oxidizer, and $NO_2$ trap). Related sample jobs, performed using the vapor sampling system (VSS) in Tanks BY-104, -105, and -106 both with and without $NO_x$ trains protected by a leading $NH_3$ trap (e.g., Clauss et al. 1994), indicated that the presence of the upstream $NH_3$ traps resulted in NO concentrations that were about 1.3- to 1.6-fold less than those from unprotected $NO_2$ traps. The $NO_2$ concentrations were also potentially less following an $NH_3$ trap.

The concentrations of $NO_2$ and NO were $\leq$ 0.02 and 0.13 ± 0.01 ppmv, respectively. Blank-corrected $NO_2^-$ quantities in the sorbent traps averaged $\leq$ 0.002 $\mu$mol ($NO_2$ samples) and 0.0119 ± 0.0009 $\mu$mol (NO samples). Nitrite blank levels used to correct data were 0.0139 ± 0.0003 $\mu$mol in front and 0.0072 ± 0.0002 $\mu$mol in back sorbent sections and were based on the analytical results from the spare/blank sorbent train. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 $\mu$mol of $NO_2^-$ during related sample jobs yielded percentage recoveries of 153 ± 14%, 103 ± 4%, 106 ± 8%, and 111 ± 7%, respectively (Clauss et al. 1994; Ligotke et al. 1994). No samples were reanalyzed to check repeatability. No sample leachates were spiked after initial analysis with quantities of $NO_2^-$ to test analytical percentage recoveries. A 4-point calibration was performed over a concentration range of 0 to 0.5 $\mu$g $NO_{2^-}$ per mL in the desorbing matrix.

**2.4.3 Gravimetric Results**. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 20 ± 10 mg/L. Excluding one sample, the result was 13 to 17 mg/L; however, no reason was found to exclude the single sample, indicating that a mass concentration of 31 mg/L existed in the vapor space. Analysis of $NH_3$ samples (2.4.1) provided an indication that the sample volumes were not the likely source of the possible error. The result was based on an average blank-corrected mass gain of 88 mg from all three sets of sample trains. The actual mass gains were corrected by subtracting a blank mass gain of 2 mg. The blank correction was determined as the average of blank sorbent trap trains from six related ISS sample jobs, a group from which the individual results ranged between - 1 and + 4 mg. The overall measurement uncertainty was estimated based on the variability of the samples and the range of blank data. Although no spiked blanks were tested, the percentage recovery of mass from three blank $H_20$ traps spiked with 51 mg water was 103 ± 2% during a related sample job (Clauss et al. 1994).

**Table 2.3** Inorganic Vapor Sample Results Obtained From *In Situ* Sampling of the Headspace of Tank TY-104 on 8/5/94

| | Analytical Results (μmol) | | | | |
|---|---|---|---|---|---|
| Sample | Front Section | Back Section | Total(b) Blank-Corrected | Sample Volume (L) | Vapor(a) Concentration (ppmv) |
| $NH_3$ Samples: | | | 8.9(c) | 4.32(c) | 50 ± 1(c) |
| S4061- 061-35W | 8.7 | ≤0.03 | 8.7 | 4.30 | 49 |
| S4061- 061-36W | 8.9 | NA(d) | 8.9 | 4.32 | 50 |
| S4061- 061-41W | 9.2 | NA | 9.2 | 4.35 | 51 |
| $NO_2$ Samples: | | | ≤0.002 | 4.32 | ≤ 0.02 |
| S4061- 061-35W | 0.0112 | 0.0068 | n/a(d) | 4.30 | n/a |
| S4061- 061-36W | 0.0143 | 0.0070 | n/a | 4.32 | n/a |
| S4061- 061-41W | 0.0147 | 0.0069 | n/a | 4.35 | n/a |
| NO Samples: | | | 0.0119 | 4.32 | 0.13 ± 0.01 |
| S4061- 061-35W | 0.0264 | 0.0073 | 0.0125 | 4.30 | 0.14 |
| S4061- 061-36W | 0.0248 | 0.0076 | 0.0109 | 4.32 | 0.12 |
| S4061- 061-41W | 0.0262 | 0.0080 | 0.0123 | 4.35 | 0.14 |
| Gravimetric Samples (mg.mg/L): | | | 88 mg | 4.32 | 20 ± 10 mg/L |
| S4061- 061-35W | n/a | n/a | 132 | 4.30 | 31 |
| S4061- 061-36W | n/a | n/a | 75 | 4.32 | 17 |
| S4061- 061-41W | n/a | n/a | 56 | 4.35 | 13 |

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(a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (corrected to 21°C and 760 torr). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrate. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks.

(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 2.4.

(c) Underlined values represent the average of the set samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples other than mass concentration. The uncertainty in mass concentration was determined based on the added uncertainty caused by the range of results of six related blanks. The use of "≤" is defined in Section 2.0.

(d) NA = not analyzed. Only selected back sorbent sections were analyzed. n/a = not applicable.

# 3.0 Organic Task

## 3.1 SUMMA™ Canister Preparation

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to PNL 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 by PNL Technical Procedure PNL-TVP-01[(b)], which is a modification of U.S. Environmental Protection Agency (EPA) compendium Method TO-14. If the canister is verified as clean, free of TO-14 and unknown contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 5 torr Hg, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 $\mu$L of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

## 3.2 Sample Analysis Method

The SUMMA™ canister sample was analyzed according to PNL Technical Procedure PNL-TVP-03 [(c)], which is a modified version of EPA compendium Method TO-14. The method uses an EnTech cryoconcentration system interfaced with either a 5971 or a 5972 Hewlett Packard (HP) benchtop GC/MS. The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate the air volume, then transfer the volume to the GC/MS for analysis. A 100-mL volume of sample is measured and analyzed from the tank headspace. The organic components in the sampled air are separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm internal diameter with 3-$\mu$m film thickness. The GC oven is programmed to run a temperature gradient beginning at 40°C, holding for 5 min, and ramping at 4°C per min to a final temperature of 260°C, with a 5-min hold. Twenty-four hours before the analysis, the SUMMA™ canister samples were pressurized with purified air (Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The starting pressure was first measured using a calibrated diaphragm gauge (Cole Parmer) then pressurized to a level exactly twice the original pressure. For example, if the canister had a starting pressure of 740 torr, it was pressurized to 1480 torr. This dilution was an effort to improve the precision of the analysis. The sample dilution was taken into account when calculating the analysis results. The instrument calibration mixture for the TO-14 analysis consists of the standard 39 organic analytes with an additional 14 tank-related compounds.

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

(b) Pacific Northwest Laboratory. 8/94. *Determination of TO-14 Volatile Organic Compounds in Ambient Air Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-01 (Rev. 0). PNL Technical Procedure, Richland, Washington.

(c) Pacific Northwest Laboratory. 8/94. *Determination of TO-14 Volatile Organic Compounds in Hanford Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-03 (Rev. 0), PNL Technical Procedure, Richland, Washington.

Together, these 53 compounds that are directly quantified in this analysis make up the target analyte list (these 53 compounds will be referred to as target analytes). The calibration mixture was prepared by blending a commercially prepared 39-compound TO-14 calibration mixture with a 14-compound mixture created using a KinTech® permeation-tube standard generation system. The operation of the permeation tube system follows the method detailed in PNL Technical Procedure PNL-TVP-06[a]. The standard calibration mix was analyzed using six aliquot sizes ranging from 5 mL to 300 mL. Depending on the concentration of each analyte in the mixture, either five or six points were used to construct the calibration curve. Butanoic acid was added to the mixture, but was not detected in the analysis. Butanal was recovered very poorly, producing a much lower than expected response. This results in a much higher measured amount reported in the sample analysis. This problem is currently under investigation. Performance-based detection limits for the target analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 ppbv is met.

## 3.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "quick tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated over 5 to 6 data points ranging from 5 ppbv to 300 ppbv, using a standard gas mixture containing 39 volatile organic compounds listed in EPA compendium Method TO-14 and an additional 14 tank-related compounds (referred to as target organic analytes). A gas mixture containing bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-$d_5$ was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration curve was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. A least-squares linear-regression routine was applied to the data set to generate the best-fit line for each compound. The equation for that line was then used to quantify the target organic analytes found in the tank samples.

The ambient air sample collected ~10 m upwind of TY-104 was used as a method blank and was used to determine the potential for analyte interferences in the samples. Continuing calibration standards for this sample set fell within ± 25% of the expected concentrations for the analytes reported.

**3.3.1 Quantitation Results of Target Organic Analytes.** The quantitative-analysis results for the target organic analytes were calculated directly from the calibration curve generated using the IS method described above and in PNL-TVP-03. The conversion from ppbv to mg/m$^3$ assumes standard

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[a] Pacific Northwest Laboratory. 8/94. *Preparation of TO-14 Volatile Organic Compounds Gas Standards*, PNL-TVP-06 (Rev. 0). PNL Technical Procedure, Richland, Washington.

temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

$$\text{mg/m}^3 = \frac{(\text{ppbv}/1000) \times \text{g mol wt of compound}}{22.4 \text{ L/mol}} \qquad (3.1)$$

**3.3.2 Identification and Quantitation of Tentatively Identified Compounds.** The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/NIST/WILEY Library, which is a part of the HP 5971/5972 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak. The concentration of each TIC was estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration in mg/m$^3$:

$$\text{Response Factor} = \frac{\text{IS conc. (mg/m}^3)}{\text{IS peak area}} \qquad (3.2)$$

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

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

$$\text{TIC in ppbv} = \frac{\text{TIC (mg/m}^3) \times 22.4 \text{ L/mol} \times 1000}{\text{TIC g mol wt}} \qquad (3.3)$$

The IS level added to all blank, standard, and sample injections was 104 ppbv for bromochloromethane, 101 ppbv for 1,4-difluorobenzene, and 98.5 ppbv for chlorobenzene-d$_5$. The IS concentrations were converted from ppbv to mg/m$^3$ at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, and 117.6 for chlorobenzene-d$_5$. All sample concentrations were multiplied by a factor of two to account for the dilution step described in Section 3.2.

## 3.4 Analysis Results

The results from the GC/MS analysis of the tank-headspace samples are presented in Tables 3.1 and 3.2. The results of replicate analyses of a single sample are presented in Table 3.3 and 3.4 The results of GC/MS analysis of an ambient-air sample collected upwind of Tank TY-104 is presented in Table 3.5. A representative total ion chromatogram showing the identity of major constituents is given in Figure 3.1.

Table 3.1 lists the quantitative results for compounds listed as target analytes. Eight analytes were above the 5-ppbv detection limit. Acetone, at 2.24 mg/m$^3$, was approximately 90% of the total concentration of target analytes. Table 3.2 lists the semi-quantitative results for the TICs. Thirty TICs were examined. Twenty-four TICs were detected in two or more SUMMA™ canisters, and these were used to determine the total TIC concentration. The total concentration of the TIC compounds was found to be 15.18 mg/m$^3$. The predominant species observed were

3-methylhexane, 2-methylhexane, and 2,3-dimethylpentane. The normal paraffin hydrocarbons (NPHs), defined as n-alkanes from $C_{11}$ to $C_{15}$, were observed.

SUMMA™ canister PNL 063 was analyzed in replicate for target analytes and TICs to determine precision. The analytical and relative percent difference (RPD) results are presented in Tables 3.3 and 3.4. The RPD was calculated for analytes detected above the detection limit and found in both replicates. Seven target analytes had an RPD of less than 10%. Twenty of the 24 TICs detected had RPDs of less than 10%. The TICs carbonyl sulfide, propane, 2-methyl-2-propanol, and tetradecane had RPDs greater than 10%.

Table 3.5 lists results of target analyte analyses for ambient air collected ~10 m upwind of Tank TY-104. The only analyte detected was 1,2,4-trichlorobenzene its concentration was 0.10 mg/m$^3$. No TICs were observed.

# 4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from *in situ* samples of the headspace of Tank TY-104 on 8/5/94. Sampling and analysis methods followed those described by Ligotke et al. (1994) for samples obtained from Tank C-103 containing a relatively complex headspace composition. Method-validation measurements during that study did appear to validate the trapping and analysis of $NH_3$, but did not eliminate the possibility of interferences that could affect $NO_x$ results. It is recommended that additional control samples be obtained if a tank is discovered in the future to contain significant quantities of $NO_x$. In the current sample job, $NO_x$ samples were obtained after first passing the sample flow through an $NH_3$ trap. The average and the standard deviation of the concentration results from inorganic sorbent trains were 50 ± 1 ppmv ($NH_3$), $\leq$0.02 ppmv ($NO_2$), 0.13 ± 0.01 ppmv (NO), and 20 ± 10 mg/L (vapor-mass concentration). The vapor-mass concentration is expected to consist largely of water vapor. The reason for the large uncertainty in mass concentration was not resolved. Uncertainties were based on one standard deviation of analytical results; information on sample-volume uncertainty was not provided. It is recommended that sample-volume uncertainties be evaluated and reported along with analytical uncertainties in subsequent sample jobs.

Organic analysis of the tank-headspace samples from Tank TY-104 identified eight target analytes above the 5-ppbv MDL and 30 TICs above the 10-ppbv detection limit. Twenty-four TICs were identified in two or more of the SUMMA™ samples. The total target analyte concentration accounted for 22% of the total compounds identified by both the target analyte and the TIC analyses. Acetone accounted for 52% of the target analytes and 12% of the total compounds identified by both analyses. The highest concentration TIC was 3-methylhexane; it accounted for 31% of the total TIC concentration. The results of the TIC analysis identified numerous NPH type compounds as the predominant species (by number) present in the tank-headspace samples. Results of replicate analysis of a single SUMMA™ canister observed seven target analytes, and 20 TICs have RPDs of less than 10%. The results of the ambient-air sample collected ~10 m upwind of Tank TY-104 identified one target analyte, 1,2,4-trichlorobenzene, and no TICs.

# 5.0 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.

Mahlum, D. 1994. *Toxicological Evaluation of Analytes from Tank 241-C-103.* PNL-10189, Pacific Northwest Laboratory, Richland, Washington.

# 6.0 Further Reading

Pacific Northwest Laboratory. Analytical Laboratory Procedure Compendium. Procedures PNL-ALO-212, -226, -271. PNL-MA-599, Richland, Washington.

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

Pacific Northwest Laboratory. Quality Assurance Plan for Activities Conducted by the Analytical Chemistry Laboratory (ACL). MCS-033, Analytical Chemistry Laboratory, Richland, Washington.

Pacific Northwest Laboratory. 1994. *Determination of TO-14 Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometry Analysis*, PNL-TVP-03 (Rev. 0), PNL Technical Procedure, Richland, Washington.

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

**Table 3.1** Positively Identified and Quantitated Target Organic Analytes(a) of Samples Collected from the Headspace of Tank TY-104 in SUMMA™ Canisters on 8/5/94

| | | | S4063—.041(b) PNL 041(d) Concentration | | S4063—.063(b),(c) PNL 063(d) Concentration | | S4063—.064(b) PNL 064(d) Concentration | | Means and Standard Deviation | |
|---|---|---|---|---|---|---|---|---|---|---|
| Analyte | CAS No. | Mol Wt | (mg/m$^3$) | (ppbv) | (mg/m$^3$) | (ppbv) | (mg/m$^3$) | (ppbv) | (mg/m$^3$) | St Dev |
| Dichlorodifluoromethane (FREON-12) | 75-71-8 | 120 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| Methyl Chloride (Chloromethane) | 74-87-3 | 50 | < 0.01 | < 5 | < 0.01 | < 5 | < 0.01 | < 5 | (e) | (e) |
| 1,2-Dichloro-1,1,2,2,-Tetrafluoroethane (FREON-114) | 76-14-2 | 170 | < 0.04 | < 5 | < 0.04 | < 5 | < 0.04 | < 5 | (e) | (e) |
| Chloroethene (Vinyl Chloride) | 75-01-4 | 64 | < 0.01 | < 5 | < 0.01 | < 5 | < 0.01 | < 5 | (e) | (e) |
| Methyl Bromide (Bromomethane) | 74-83-9 | 94 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| Ethyl Chloride | 75-00-3 | 62 | < 0.01 | < 5 | < 0.01 | < 5 | < 0.01 | < 5 | (e) | (e) |
| Trichlorofluoromethane (FREON-11) | 75-69-4 | 136 | 0.43 | 70.1 | 0.4 | 65.9 | 0.44 | 71.7 | 0.42 | 0.02 |
| 1,1-Dichloroethene (1,1-Dichloroethylene) | 75-35-4 | 96 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| Dichloromethane (Methylene Chloride) | 75-09-2 | 84 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| 1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON-113) | 76-13-1 | 186 | 0.48 | 57.1 | 0.44 | 52.6 | 0.45 | 54.0 | 0.46 | 0.02 |
| 1,1-Dichloroethane | 75-34-3 | 98 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| cis-1,2-Dichloroethene (cis-1,2-Dichloroethylene) | 156-59-2 | 96 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| Trichloromethane (Chloroform) | 67-66-3 | 118 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| 1,2-Dichloroethane | 107-06-2 | 98 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| 1,1,1-Trichloroethane | 71-55-6 | 132 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| Benzene | 71-43-2 | 78 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| Carbon Tetrachloride | 56-23-5 | 152 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| 1,2-Dichloropropane | 78-87-5 | 112 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| Trichloroethylene | 79-01-6 | 130 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| cis 1,3-Dichloropropene | 10061-01-5 | 110 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| trans 1,3-Dichloropropene | 10061-02-6 | 110 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| 1,1,2-Trichloroethane | 79-00-5 | 132 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| Methyl Benzene (Toluene) | 108-88-3 | 92 | 0.31 | 74.4 | 0.26 | 63.2 | 0.26 | 63.9 | 0.28 | 0.03 |
| 1,2-Dibromoethane | 106-93-4 | 186 | < 0.04 | < 5 | < 0.04 | < 5 | < 0.04 | < 5 | (e) | (e) |
| Tetrachloroethene (Perchloroethylene) | 127-18-4 | 164 | < 0.04 | < 5 | < 0.04 | < 5 | < 0.04 | < 5 | (e) | (e) |
| Chlorobenzene | 108-90-7 | 112 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| Ethylbenzene | 100-41-4 | 106 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| m-Xylene (1,3-Dimethylbenzene)(f) | 108-38-3 | 106 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| p-Xylene (1,4-Dimethylbenzene)(f) | 106-42-3 | 106 | | | | | | | | |
| Styrene | 100-42-5 | 104 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 166 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| o-Xylene (1,2-Dimethylbenzene) | 95-47-6 | 106 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |

## TY-104 Table 3.1 (Contd)

| | | | S4063—.041[b] PNL 041[d] Concentration | | S4063—.063[b],[c] PNL 063[d] Concentration | | S4063—.064[b] PNL 064[d] Concentration | | Means and Standard Deviation | |
|---|---|---|---|---|---|---|---|---|---|---|
| Analyte | CAS No. | Mol Wt | ($mg/m^3$) | (ppbv) | ($mg/m^3$) | (ppbv) | ($mg/m^3$) | (ppbv) | ($mg/m^3$) | St Dev |
| 1,3,5-Trimethylbenzene | 108-67-8 | 120 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| 1,2,4-Trimethylbenzene | 95-63-6 | 120 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| Chloromethylbenzene, alpha (Benzyl Chloride) | 100-44-7 | 126 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| m-Dichlorobenzene (1,3-Dichlorobenzene) | 541-73-1 | 146 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| p-Dichlorobenzene (1,4-Dichlorobenzene) | 106-46-7 | 146 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| o-Dichlorobenzene (1,2-Dichlorobenzene) | 95-50-1 | 146 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| 1,2,4-Trichlorobenzene | 120-82-1 | 180 | < 0.04 | < 5 | < 0.04 | < 5 | < 0.04 | < 5 | (e) | (e) |
| Hexachloro-1,3-Butadiene | 87-68-3 | 258 | < 0.60 | < 5 | < 0.60 | < 5 | < 0.60 | < 5 | (e) | (e) |
| 2-Butanone | 78-93-3 | 72 | 0.05 | 14.8 | 0.04 | 13.6 | 0.04 | 12.3 | 0.04 | 1.29 |
| Acetone | 67-64-1 | 58 | 2.27 | 877 | 2.30 | 886 | 2.14 | 825 | 2.2 | 1.19 |
| Acetonitrile | 75-05-8 | 41 | 0.17 | 94.1 | 0.13 | 70.1 | 0.15 | 83.9 | 0.15 | 0.02 |
| Heptane | 142-82-5 | 100 | 0.71 | 158 | 0.63 | 140 | 0.59 | 133 | 0.64 | 0.06 |
| Tetrahydrofuran | 109-99-9 | 72 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| Pyridine | 110-86-1 | 79 | < 0.02 | < 5 | 0.16 | 44.0 | < 0.02 | < 5 | (e) | (e) |
| Butanenitrile | 109-74-0 | 69 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| Cyclohexane | 110-82-7 | 84 | 0.01 | 3.8 | < 0.02 | < 5 | 0.01 | 3.0 | 0.06 | (e) |
| Decane | 124-18-5 | 142 | < 0.03 | < 5 | < 0.03 | < 5 | < 0.03 | < 5 | (e) | (e) |
| Hexane | 110-54-3 | 86 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| 4-Methyl-2-Pentanone | 108-10-1 | 100 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| Propanenitrile | 107-12-0 | 55 | < 0.01 | < 5 | < 0.01 | < 5 | < 0.01 | < 5 | (e) | (e) |
| Cyclohexanone | 108-94-1 | 98 | < 0.02 | < 5 | < 0.02 | < 5 | < 0.02 | < 5 | (e) | (e) |
| Propanol | 71-23-8 | 60 | < 0.01 | < 5 | < 0.01 | < 5 | < 0.01 | < 5 | (e) | (e) |

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(a) TO-14 plus 14 additonal target analytes.
(b) WHC sample identification number.
(c) PNL canister number.
(d) Replicates of this sample are found in Table 3.3
(e) Average and/or standard deviation are not meaningful for this analyte.
(f) m-Xylene and p-Xylene coelute; the reported concentration is the sum of these two compounds.

**Table 3.2** Tentatively Identified Compounds and Estimated Concentrations[a] of Samples from the Headspace of Tank TY-104 in SUMMA™ Canisters Collected on 8/5/94

| Tentatively Identified Compound[e] | CAS No.[e] | Mol Wt | Ret Time | S4063—.041[b] PNL 041[d] |  | S4082—.063[b],[c] PNL 063[d] |  | S4082—.064[b] PNL 064[d] |  | Means and Standard Deviations |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | ($mg/m^3$) | (ppbv) | ($mg/m^3$) | (ppbv) | ($mg/m^3$) | (ppbv) | ($mg/m^3$) | St Dev | (ppbv) | St Dev |
| Carbonyl sulfide | 463-58-1 | 60 | 3.9 | 0.03 | 9.3 | 0.03 | 11.2 | 0.03 | 9.7 | 0.03 | 0.00 | 10.1 | 1.0 |
| Propane | 74-98-6 | 44 | 3.9 | 0.03 | 13.2 | 0.01 | 2.5 | 0.02 | 10.7 | 0.02 | 0.01 | 8.8 | 5.6 |
| Acetaldehyde | 75-07-0 | 44 | 5.1 | 0.06 | 30.0 | 0.06 | 29.5 | 0.06 | 32.1 | 0.06 | 0.00 | 30.5 | 1.3 |
| Isopropyl alcohol | 67-63-0 | 60 | 9.0 | < 0.03 | < 10 | 0.06 | 20.9 | 0.05 | 20.2 | 0.06 | (f) | 20.5 | (f) |
| Methyl nitrate | 598-58-3 | 77 | 10.3 | 0.11 | 32.3 | 0.11 | 30.5 | 0.11 | 31.4 | 0.11 | 0.00 | 31.4 | 0.9 |
| 2-Methyl-2-propenal | 78-85-3 | 70 | 12.1 | < 0.03 | < 10 | 0.08 | 25.9 | < 0.03 | < 10 | (f) | (f) | (f) | (f) |
| 3-Methylpentane | 96-14-0 | 86 | 13.8 | 0.06 | 16.7 | 0.06 | 14.6 | 0.05 | 14.1 | 0.06 | 0.01 | 15.1 | 1.4 |
| Ethylnitrate | 625-58-1 | 91 | 14.9 | 0.10 | 25.4 | 0.10 | 24.1 | 0.10 | 23.6 | 0.10 | 0.00 | 24.4 | 0.9 |
| 2-Methyl-1-propanol | 78-83-1 | 74 | 15.5 | < 0.03 | < 10 | 0.06 | 18.8 | < 0.03 | < 10 | (f) | (f) | (f) | (f) |
| Unknown C7 Alkane |  | 100 | 16.1 | 0.19 | 43.5 | 0.17 | 38.5 | 0.16 | 36.3 | 0.18 | 0.02 | 39.4 | 3.7 |
| 2,4-Dimethylpentane | 108-08-7 | 100 | 16.4 | < 0.04 | < 10 | 0.20 | 45.5 | 0.19 | 42.1 | 0.20 | (f) | 43.8 | (f) |
| Unknown C7 Alkane |  | 100 | 16.4 | 0.23 | 50.8 | < 0.04 | < 10 | < 0.04 | < 10 | (f) | (f) | (f) | (f) |
| Unknown C7 Alkane |  | 100 | 16.9 | < 0.04 | < 10 | 0.09 | 19.5 | 0.08 | 18.8 | 0.09 | (f) | 19.2 | (f) |
| 2,2,3-Trimethylbutane | 464-06-2 | 100 | 16.9 | 0.10 | 21.7 | < 0.04 | < 10 | < 0.04 | < 10 | (f) | (f) | (f) | (f) |
| 1-Butanol | 71-36-3 | 74 | 17.4 | 0.24 | 71.7 | 0.23 | 68.1 | 0.23 | 68.7 | 0.23 | 0.01 | 69.5 | 1.9 |
| 3,3-Dimethylpentane | 562-49-2 | 100 | 18.0 | 1.16 | 259 | 1.02 | 229 | 0.95 | 214 | 1.04 | 0.10 | 234 | 23.0 |
| 2-Methylhexane | 591-76-4 | 100 | 18.5 | 3.12 | 698 | 2.78 | 622 | 2.66 | 596 | 2.85 | 0.24 | 639 | 53.2 |
| 2,3-Dimethylpentane | 565-59-3 | 100 | 18.7 | 2.63 | 588 | 2.30 | 516 | 2.16 | 484 | 2.36 | 0.24 | 529 | 53.7 |
| 3-Methylhexane | 589-34-4 | 100 | 19.0 | 5.14 | 1152 | 4.57 | 1024 | 4.33 | 970 | 4.68 | 0.42 | 1048 | 93.4 |
| 3-Ethylpentane | 617-78-7 | 100 | 19.7 | 1.07 | 241 | 0.95 | 212 | 0.89 | 200 | 0.97 | 0.09 | 218 | 20.8 |
| 1,2-Dimethylcyclopentane | 2452-99-5 | 98 | 19.9 | 0.24 | 55.1 | 0.22 | 49.4 | 0.21 | 47.3 | 0.22 | 0.02 | 50.6 | 4.0 |
| Unknown C8 Alkane |  | 114 | 21.7 | 0.09 | 16.7 | 0.07 | 13.6 | 0.07 | 13.4 | 0.07 | 0.01 | 14.5 | 1.9 |
| Methylcyclohexane | 108-87-2 | 98 | 21.9 | 1.23 | 280 | < 0.04 | < 10 | 1.07 | 243 | 1.15 | (f) | 262 | (f) |
| 2,4-Dimethylhexane | 589-43-5 | 114 | 22.3 | < 0.05 | < 10 | < 0.05 | < 10 | 0.08 | 14.7 | (f) | (f) | (f) | (f) |
| Unknown C8 Alkane |  | 114 | 22.4 | 0.09 | 17.3 | 0.07 | 12.8 | < 0.05 | < 10 | 0.08 | 0.02 | 15.0 | 3.2 |
| 2-Ethyl-1-hexanol | 104-76-7 | 130 | 36.3 | 0.19 | 32.4 | 0.05 | 9.0 | < 0.06 | < 10 | 0.12 | (f) | 20.7 | (f) |
| Acetophenone | 98-86-2 | 120 | 38.0 | 0.05 | 9.5 | < 0.05 | < 10 | < 0.05 | < 10 | (f) | (f) | (f) | (f) |

## TY-104 Table 3.2 (Contd)

| Tentatively Identified Compound[e] | CAS No.[e] | Mol Wt | Ret Time | S4063—.041[b] PNL 041[d] |  | S4082—.063[b],[c] PNL 063[d] |  | S4082—.064[b] PNL 064[d] |  | Means and Standard Deviations |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | (mg/m$^3$) | (ppbv) | (mg/m$^3$) | (ppbv) | (mg/m$^3$) | (ppbv) | (mg/m$^3$) | St Dev | (ppbv) | St Dev |
| Dodecane | 112-40-3 | 170 | 44.1 | 0.13 | 16.6 | 0.11 | 15.0 | 0.09 | 12.0 | 0.11 | 0.02 | 14.5 | 2.3 |
| Tridecane | 629-50-5 | 184 | 47.8 | 0.42 | 50.8 | 0.36 | 44.2 | 0.21 | 25.1 | 0.33 | 0.11 | 40.0 | 13.3 |
| Tetradecane | 629-59-4 | 198 | 51.4 | 0.09 | 10.6 | 0.07 | 8.1 | < 0.09 | < 10 | 0.08 | (f) | 9.4 | (f) |

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(a) Semi-quantitative estimate calculated using concentration of closest eluting ID.
(b) WHC sample identification number.
(c) Replicates of this sample are found in Table 3.4
(d) PNL SUMMA$^{TM}$ canister number.
(e) Obtained by mass spectral interpretation amd comparison with the EPA/NIST/WILEY Library.
(f) Average and/or standard deviation are not meaningful for this analyte.

**Table 3.3** Positively Identified and Quantitated Target Organic Analytes[a] of Replicate Analyses of a Single SUMMA™ Canister Collected from the Headspace of Tank TY-104 on 8/5/94

| | | | S4063—.063[b]<br>PNL 063[c]<br>Concentration | | S4063—.063[b]<br>PNL 063[c]<br>Concentration | | Relative<br>Percent<br>Difference |
|---|---|---|---|---|---|---|---|
| Analyte | CAS No. | Mol Wt | ($mg/m^3$) | (ppbv) | ($mg/m^3$) | (ppbv) | % |
| Dichlorodifluoromethane (FREON-12) | 75-71-8 | 120 | < 0.03 | < 5 | < 0.03 | < 5 | |
| Methyl Chloride (Chloromethane) | 74-87-3 | 50 | < 0.01 | < 5 | < 0.01 | < 5 | |
| 1,2-Dichloro-1,1,2,2,-Tetrafluoroethane (FREON-114) | 76-14-2 | 170 | < 0.04 | < 5 | < 0.04 | < 5 | |
| Chloroethene (Vinyl Chloride) | 75-01-4 | 64 | < 0.01 | < 5 | < 0.01 | < 5 | |
| Methyl Bromide (Bromomethane) | 74-83-9 | 94 | < 0.02 | < 5 | < 0.02 | < 5 | |
| Ethyl Chloride | 75-00-3 | 62 | < 0.01 | < 5 | < 0.01 | < 5 | |
| Trichlorofluoromethane (FREON-11) | 75-69-4 | 136 | 0.4 | 65.9 | 0.39 | 64.3 | 2.5 |
| 1,1-Dichloroethene (1,1-Dichloroethylene) | 75-35-4 | 96 | < 0.02 | < 5 | < 0.02 | < 5 | |
| Dichloromethane (Methylene Chloride) | 75-09-2 | 84 | < 0.02 | < 5 | < 0.02 | < 5 | |
| 1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON-113) | 76-13-1 | 186 | 0.44 | 52.6 | 0.43 | 51.1 | 2.3 |
| 1,1-Dichloroethane | 75-34-3 | 98 | < 0.02 | < 5 | < 0.02 | < 5 | |
| cis-1,2-Dichloroethene (cis-1,2-Dichloroethylene) | 156-59-2 | 96 | < 0.02 | < 5 | < 0.02 | < 5 | |
| Trichloromethane (Chloroform) | 67-66-3 | 118 | < 0.02 | < 5 | < 0.02 | < 5 | |
| cis 1,2-Dichloroethane | 107-06-2 | 98 | < 0.02 | < 5 | < 0.02 | < 5 | |
| 1,1,1-Trichloroethane | 71-55-6 | 132 | < 0.03 | < 5 | < 0.03 | < 5 | |
| Benzene | 71-43-2 | 78 | < 0.02 | < 5 | < 0.02 | < 5 | |
| Carbon Tetrachloride | 56-23-5 | 152 | < 0.03 | < 5 | < 0.03 | < 5 | |
| 1,2-Dichloropropane | 78-87-5 | 112 | < 0.03 | < 5 | < 0.03 | < 5 | |
| Trichloroethylene | 79-01-6 | 130 | < 0.03 | < 5 | < 0.03 | < 5 | |
| cis 1,3-Dichloropropene | 10061-01-5 | 110 | < 0.02 | < 5 | < 0.02 | < 5 | |
| trans 1,3-Dichloropropene | 10061-02-6 | 110 | < 0.02 | < 5 | < 0.02 | < 5 | |
| 1,1,2-Trichloroethane | 79-00-5 | 132 | < 0.03 | < 5 | < 0.03 | < 5 | |
| Methyl Benzene (Toluene) | 108-88-3 | 92 | 0.26 | 63.2 | 0.24 | 57.8 | 8.0 |
| 1,2-Dibromoethane | 106-93-4 | 186 | < 0.04 | < 5 | < 0.04 | < 5 | |
| Tetrachloroethene (Perchloroethylene) | 127-18-4 | 164 | < 0.04 | < 5 | < 0.04 | < 5 | |
| Chlorobenzene | 108-90-7 | 112 | < 0.03 | < 5 | < 0.03 | < 5 | |
| Ethylbenzene | 100-41-4 | 106 | < 0.02 | < 5 | < 0.02 | < 5 | |
| m-Xylene (1,3-Dimethylbenzene)[d] | 108-38-3 | 106 | < 0.02 | < 5 | < 0.02 | < 5 | |
| p-Xylene (1,4-Dimethylbenzene)[d] | 106-42-3 | 106 | | | | | |
| Styrene | 100-42-5 | 104 | < 0.02 | < 5 | < 0.02 | < 5 | |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 166 | < 0.02 | < 5 | < 0.02 | < 5 | |
| o-Xylene (1,2-Dimethylbenzene) | 95-47-6 | 106 | < 0.02 | < 5 | < 0.02 | < 5 | |

## TY-104 Table 3.3 (Contd)

| | | | S4063—.063[b]<br>PNL 063[c]<br>Concentration | | S4063—.063[b]<br>PNL 063[c]<br>Concentration | | Relative Percent Difference |
|---|---|---|---|---|---|---|---|
| Analyte | CAS No. | Mol Wt | (mg/m$^3$) | (ppbv) | (mg/m$^3$) | (ppbv) | % |
| 1,3,5-Trimethylbenzene | 108-67-8 | 120 | < 0.03 | < 5 | < 0.03 | < 5 | |
| 1,2,4-Trimethylbenzene | 95-63-6 | 120 | < 0.03 | < 5 | < 0.03 | < 5 | |
| Chloromethylbenzene, alpha (Benzyl Chloride) | 100-44-7 | 126 | < 0.03 | < 5 | < 0.03 | < 5 | |
| m-Dichlorobenzene (1,3-Dichlorobenzene) | 541-73-1 | 146 | < 0.03 | < 5 | < 0.03 | < 5 | |
| p-Dichlorobenzene (1,4-Dichlorobenzene) | 106-46-7 | 146 | < 0.03 | < 5 | < 0.03 | < 5 | |
| o-Dichlorobenzene (1,2-Dichlorobenzene) | 95-50-1 | 146 | < 0.03 | < 5 | < 0.03 | < 5 | |
| 1,2,4-Trichlorobenzene | 120-82-1 | 180 | < 0.04 | < 5 | < 0.04 | < 5 | |
| Hexachloro-1,3-Butadiene | 87-68-3 | 258 | < 0.60 | < 5 | < 0.60 | < 5 | |
| 2-Butanone | 78-93-3 | 72 | 0.04 | 13.6 | 0.04 | 13.0 | 0.0 |
| Acetone | 67-64-1 | 58 | 2.30 | 886 | 2.17 | 837 | 5.8 |
| Acetonitrile | 75-05-8 | 41 | 0.13 | 70.1 | 0.12 | 65.9 | 8.0 |
| Butanal | 123-72-8 | 72 | < 0.02 | < 5 | < 0.02 | < 5 | |
| Heptane | 142-82-5 | 100 | 0.63 | 140 | 0.59 | 133 | 6.6 |
| Tetrahydrofuran | 109-99-9 | 72 | < 0.02 | < 5 | < 0.02 | < 5 | |
| Pyridine | 110-86-1 | 79 | 0.16 | 44.0 | < 0.02 | < 5 | |
| Butanenitrile | 109-74-0 | 69 | < 0.02 | < 5 | < 0.02 | < 5 | |
| Cyclohexane | 110-82-7 | 84 | < 0.02 | < 5 | 0.01 | 2.9 | |
| Decane | 124-18-5 | 142 | < 0.03 | < 5 | < 0.03 | < 5 | |
| Hexane | 110-54-3 | 86 | < 0.02 | < 5 | < 0.02 | < 5 | |
| 4-Methyl-2-Pentanone | 108-10-1 | 100 | < 0.02 | < 5 | < 0.02 | < 5 | |
| Propanenitrile | 107-12-0 | 55 | < 0.01 | < 5 | < 0.01 | < 5 | |
| Cyclohexanone | 108-94-1 | 98 | < 0.02 | < 5 | < 0.02 | < 5 | |
| Propanol | 71-23-8 | 60 | < 0.01 | < 5 | < 0.01 | < 5 | |

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(a) TO-14 plus 14 additonal target analytes.

(b) WHC sample identification number.

(c) PNL canister number.

(d) m-Xylene and p-Xylene coelute; the reported concentration is the sum of these two compounds.

**Table 3.4** Tentatively Identified Compounds and Estimated Concentrations[a] of Replicate Analyses of a Single SUMMA™ Canister Collected from the Headspace of Tank TY-104 on 8/5/94

| Tentatively Identified Compound[d] | CAS No.[d] | Mol Wt | Ret Time | S4063----.063[b] PNL 063[c] (mg/m$^3$) | S4063----.063[b] PNL 063[c] (ppbv) | S4063----.063[b] PNL 063[c] (mg/m$^3$) | S4063----.063[b] PNL 063[c] (ppbv) | Relative Percent Difference % |
|---|---|---|---|---|---|---|---|---|
| Carbonyl sulfide | 463-58-1 | 60 | 3.9 | 0.03 | 11.2 | 0.03 | 12.7 | 12.5 |
| Propane | 74-98-6 | 44 | 3.9 | 0.01 | 2.5 | 0.02 | 11.7 | 129 |
| Acetaldehyde | 75-07-0 | 44 | 5.1 | 0.06 | 29.5 | 0.06 | 30.5 | 3.4 |
| Isopropyl alcohol | 67-63-0 | 60 | 9.0 | 0.06 | 20.9 | 0.05 | 19.8 | 5.5 |
| Methyl nitrate | 598-58-3 | 77 | 10.3 | 0.11 | 30.5 | 0.11 | 32.6 | 6.5 |
| 2-Methyl-2-propenal | 78-85-3 | 70 | 12.1 | 0.08 | 25.9 | 0.07 | 23.4 | 10.4 |
| 3-Methylpentane | 96-14-0 | 86 | 13.8 | 0.06 | 14.6 | <0.04 | <10 | |
| Ethylnitrate | 625-58-1 | 91 | 14.9 | 0.10 | 24.1 | 0.09 | 22.9 | 5.2 |
| 2-Methyl-1-propanol | 78-83-1 | 74 | 15.5 | 0.06 | 18.8 | 0.06 | 18.5 | 1.6 |
| Unknown C7 Alkane | | 100 | 16.1 | 0.17 | 38.5 | 0.17 | 38.1 | 1.2 |
| 2,4-Dimethylpentane | 108-08-7 | 100 | 16.4 | 0.20 | 45.5 | 0.19 | 42.8 | 6.1 |
| Unknown C7 Alkane | | 100 | 16.4 | <0.04 | <10 | <0.04 | <10 | |
| Unknown C7 Alkane | | 100 | 16.9 | 0.09 | 19.5 | 0.08 | 18.6 | 4.7 |
| 2,2,3-Trimethylbutane | 464-06-2 | 100 | 16.9 | <0.04 | <10 | <0.04 | <10 | |
| 1-Butanol | 71-36-3 | 74 | 17.4 | 0.23 | 68.1 | 0.22 | 67.8 | 0.4 |
| 3,3-Dimethylpentane | 562-49-2 | 100 | 18.0 | 1.02 | 229 | 0.98 | 219 | 4.7 |
| 2-Methylhexane | 591-76-4 | 100 | 18.5 | 2.78 | 622 | 2.67 | 598 | 3.9 |
| 2,3-Dimethylpentane | 565-59-3 | 100 | 18.7 | 2.30 | 516 | 2.20 | 492 | 4.8 |
| 3-Methylhexane | 589-34-4 | 100 | 19.0 | 4.57 | 1024 | 4.37 | 978 | 4.6 |
| 3-Ethylpentane | 617-78-7 | 100 | 19.7 | 0.95 | 212 | 0.90 | 202 | 4.6 |
| 1,2-Dimethylcyclopentane | 2452-99-5 | 98 | 19.9 | 0.22 | 49.4 | 0.21 | 47.3 | 4.3 |
| Unknown C8 Alkane | | 114 | 21.7 | 0.07 | 13.6 | 0.07 | 13.2 | 2.9 |
| Methylcyclohexane | 108-87-2 | 98 | 21.9 | 1.09 | 250 | 1.05 | 239 | 4.4 |
| 2,4-Dimethylhexane | 589-43-5 | 114 | 22.3 | <0.05 | <10 | 0.07 | 13.0 | |
| Unknown C8 Alkane | | 114 | 22.4 | 0.07 | 12.8 | <0.05 | <10 | |
| 2-Ethyl-1-hexanol | 104-76-7 | 130 | 36.3 | 0.05 | 9.0 | 0.05 | 8.4 | 5.9 |

**TY-104 Table 3.4 (Contd)**

| Tentatively Identified Compound[d] | CAS No.[d] | Mol Wt | Ret Time | S4063----.063[b] PNL 063[c] (mg/m³) | | S4063----.063[b] PNL 063[c] (mg/m³) | | Relative Percent Difference |
|---|---|---|---|---|---|---|---|---|
| | | | | (mg/m³) | (ppbv) | (mg/m³) | (ppbv) | % |
| Acetophenone | 98-86-2 | 120 | 38.0 | < 0.05 | < 10 | < 0.05 | < 10 | |
| Dodecane | 112-40-3 | 170 | 44.1 | 0.11 | 15.0 | 0.11 | 14.5 | 3.6 |
| Tridecane | 629-50-5 | 184 | 47.8 | 0.36 | 44.2 | 0.35 | 43.1 | 2.5 |
| Tetradecane | 629-59-4 | 198 | 51.4 | 0.07 | 8.1 | 0.09 | 9.7 | 17.7 |

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(a) Semi-quantitative estimate calculated using concentration of closest eluting ID.

(b) WHC sample identification number.

(c) PNL SUMMA™ canister number.

(d) Obtained by mass spectral interpretation amd comparison with the EPA/NIST/WILEY Library.

(e) No molecular weight available for calculation.

**Table 3.5** Positively Identified and Quantitated Target Organic Analytes[a] for Ambient Air Collected Near Tank TY-104 in a SUMMA™ Canister on 8/5/94

| | | | S4063----.164[b]<br>PNL 164[c]<br>Concentration | |
|---|---|---|---|---|
| Analyte | CAS No. | Mol Wt | (mg/m$^3$) | (ppbv) |
| 1,2,4-Trichlorobenzene | 120-82-1 | 181 | 0.10 | 12.6 |

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(a) TO-14 plus 14 additonal analytes.
(b) WHC sample identification number.
(c) PNL canister number.

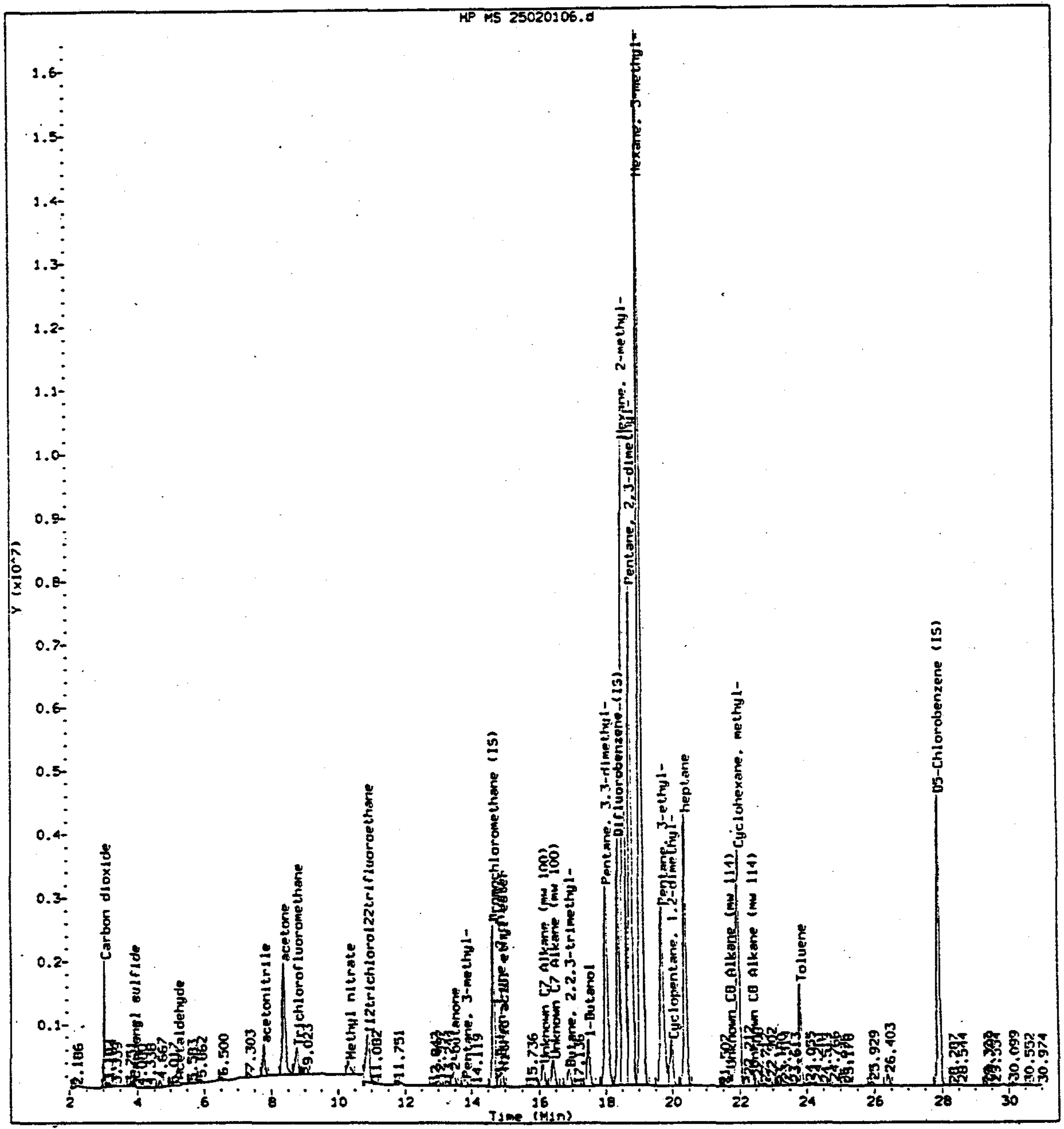

**Figure 3.1a** Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank TY-104 SUMMA™ Canister Sample S4063-___.041 Collected on 8/5/94

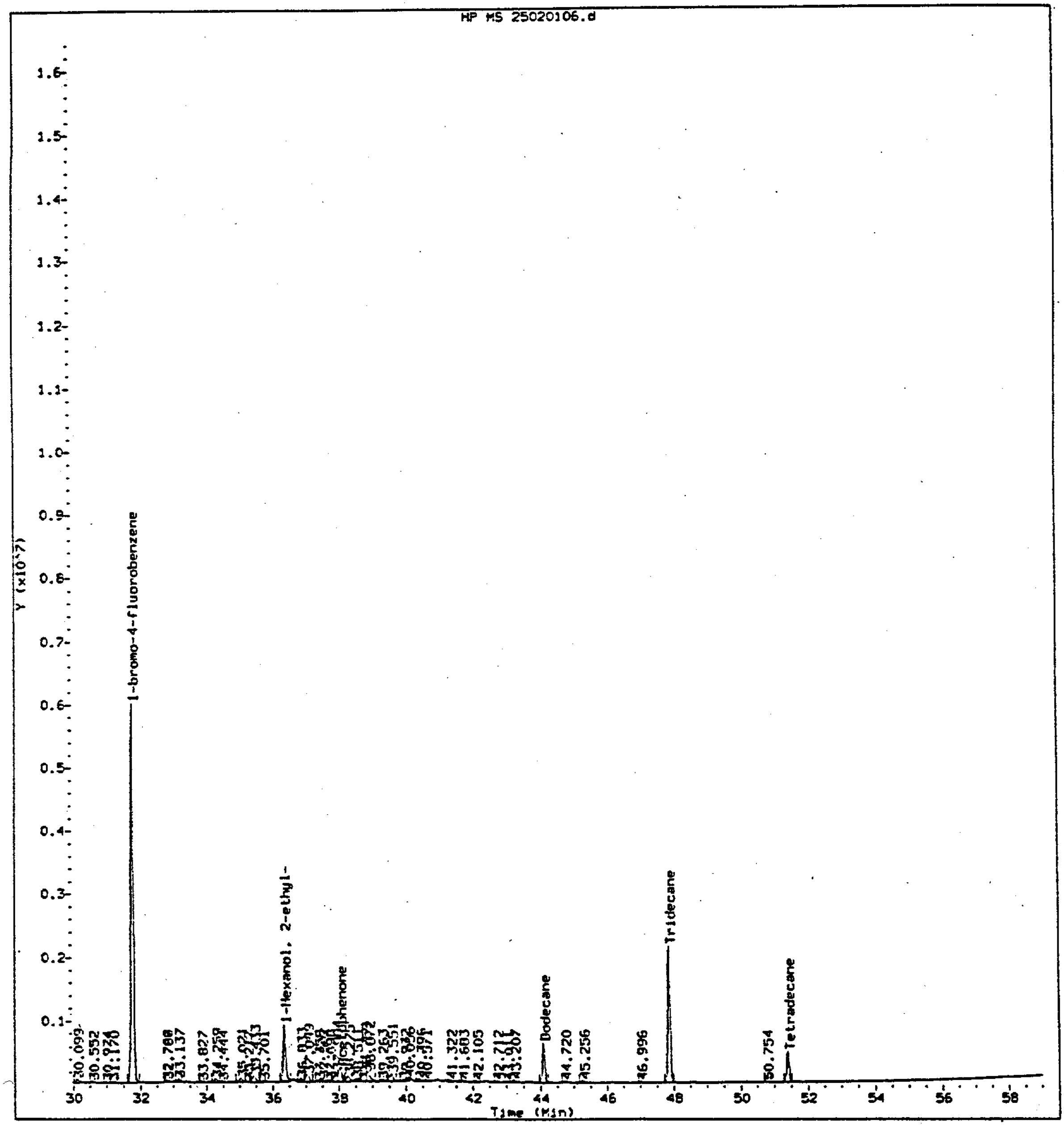

**Figure 3.1b** Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank TY-104 SUMMA™ Canister Sample S4063-___.041 Collected on 8/5/94

PNL-10737
UC-606

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B. D. McVeety, K6-84
K. B. Olsen, K6-96
J. S. Fruchter, K6-96
S. C. Goheen, P8-08
M. W. Ligotke P7-59 (6)
J. L. Huckaby, K6-55
K. L. Silvers, P7-27
Technical Report Files (5)