

**Waste Tank Vapor Characterization
Project: Annual Status Report for
FY 1995**

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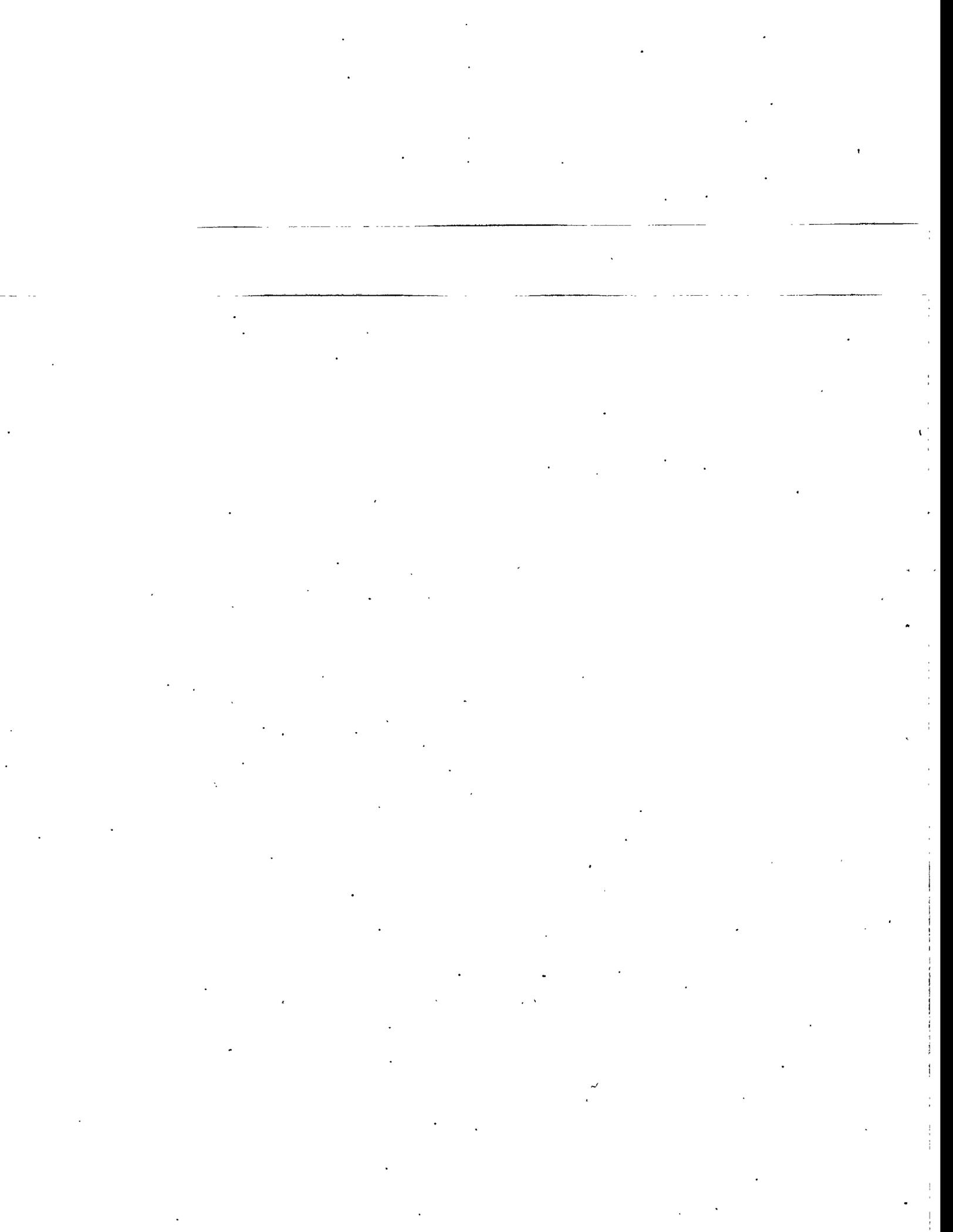
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Summary

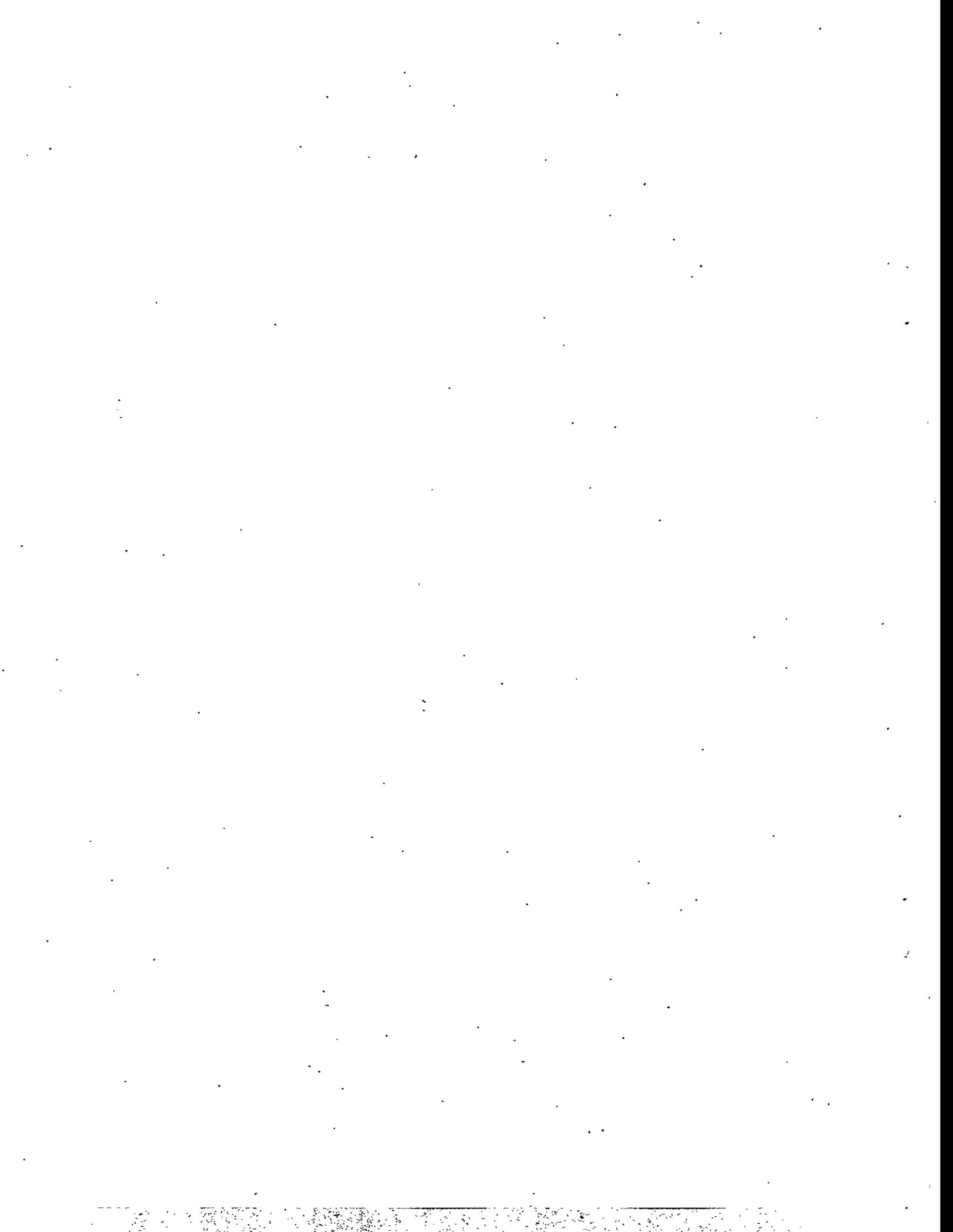
In Fiscal Year (FY) 1995, staff at the Vapor Analytical Laboratory (VAL) at Pacific Northwest National Laboratory (PNL) performed work in support of characterizing the vapor composition of the headspaces of radioactive waste tanks at the Hanford Site in Southeastern Washington. The work was supported by the Westinghouse Hanford Company (WHC) Tank Waste Remediation System (TWRS) Characterization Program and the U.S. Department of Energy's Richland Operations Office (DOE/RL). Work performed included support for technical issues and sampling methodologies, upgrades for analytical equipment, analytical method development, preparation of unexposed samples, analyses of tank headspace samples, preparation of data reports, preparation of input for WHC tank characterization reports, and operation of the tank vapor database. Work performed in FY 1995 was a continuation of work initiated with the first vapor sample job, which was performed in December 1993.

Progress made in FY 1995 included completion of sample analyses from all 40 jobs performed during the year, plus back-logged sample sets from jobs performed in FY 1994. Of the 77 vapor sample jobs performed in FY 1994 and FY 1995, reports were completed and issued for 27 by September 1995, and preparations were made to issue an additional 35 reports in October and November 1995. Final verification of data sets from samples received in late FY 1995 and issuance of the remaining 15 data reports are scheduled to be completed in December 1995 and January 1996. In addition, preparations were made to continue operations in FY 1996, including support for technical basis issues, enhanced quality assurance controls, new analytical methods, in-tank comparisons of vehicle- and cart-based sampling systems, studies of seasonal changes in the composition of tank headspace vapors, a streamlined data reporting process, and continued loading of data into the tank vapor database.



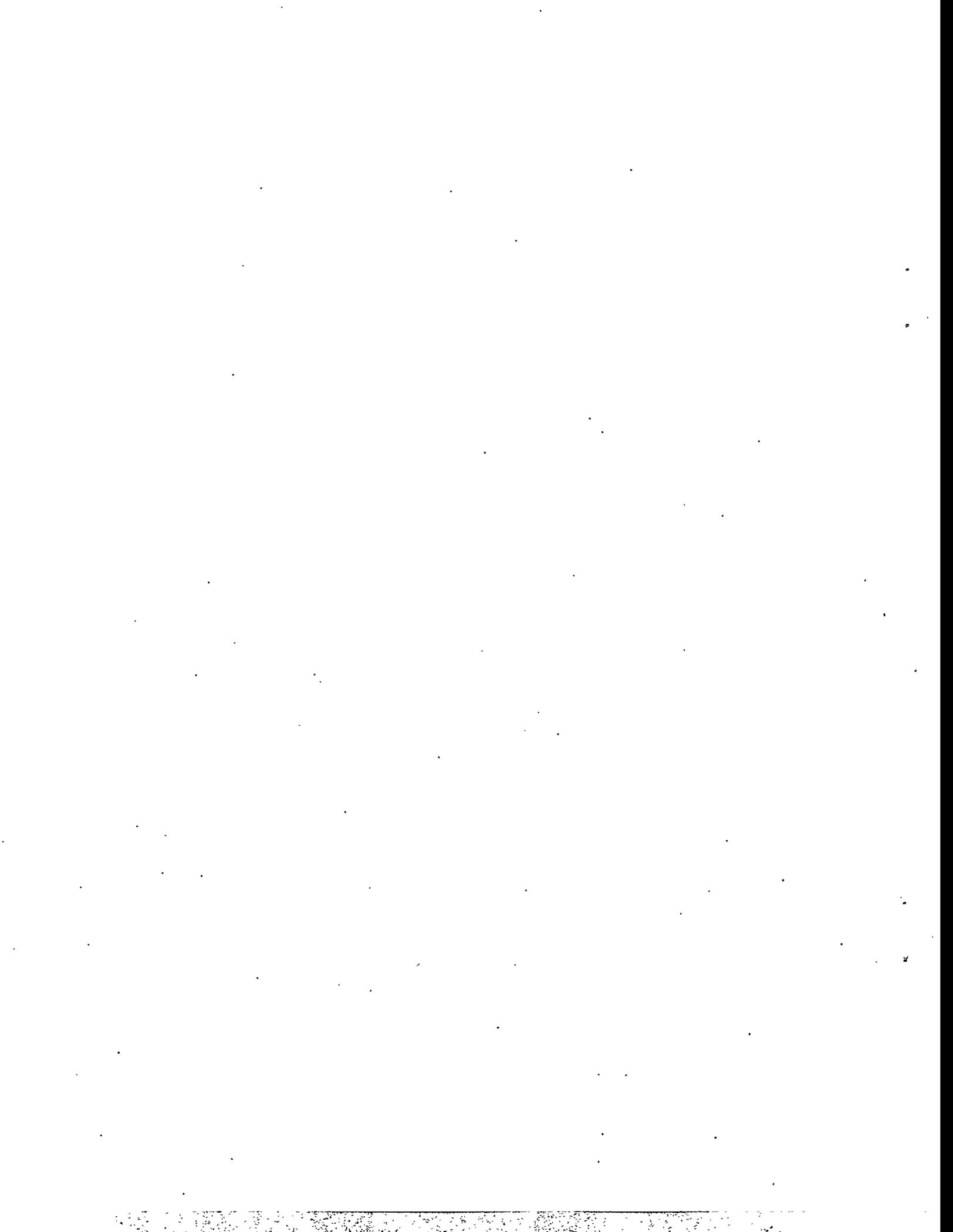
Acknowledgments

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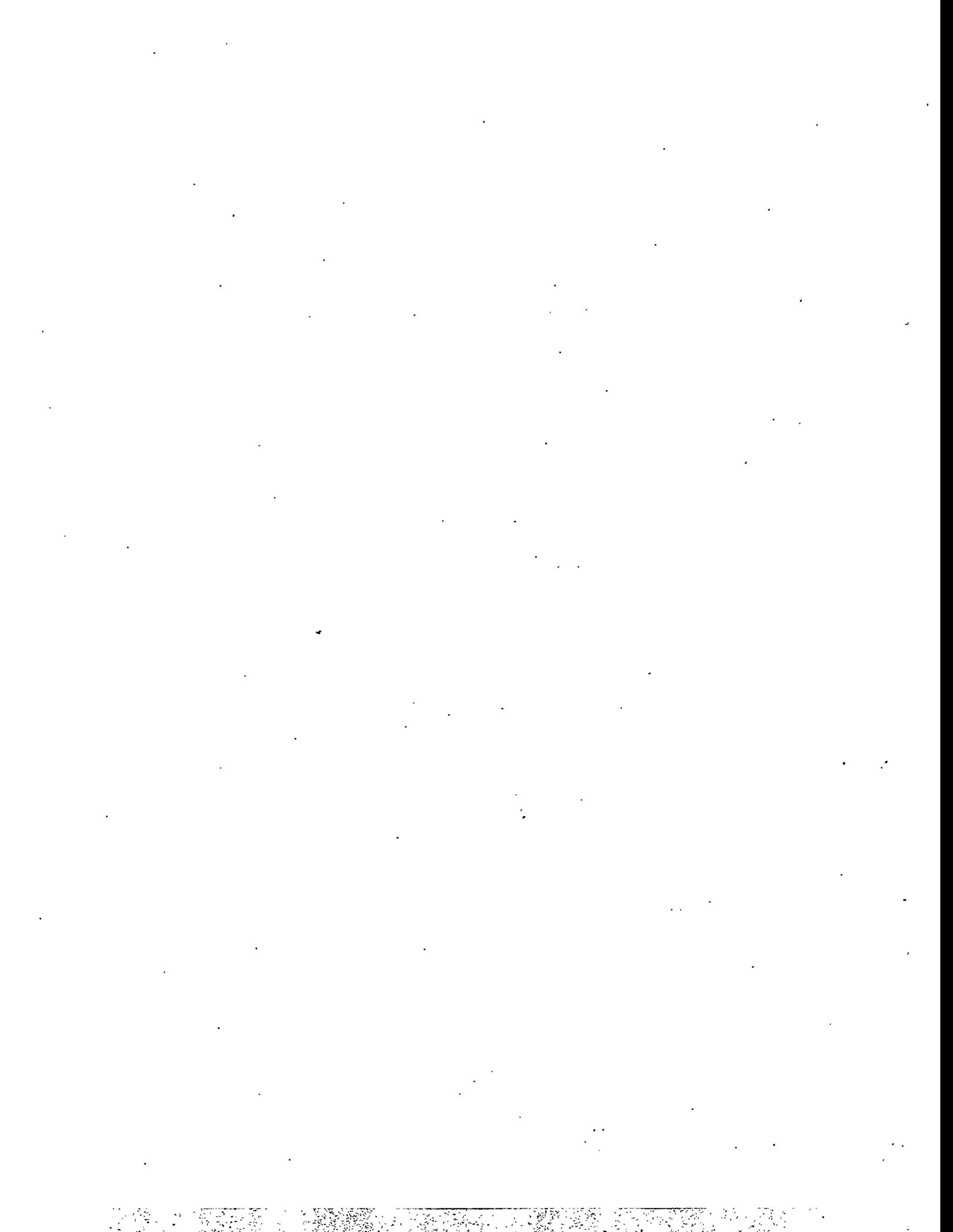
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Abbreviations

CAS	Chemical Abstracts Service
COC	Chain of custody
C _v	Concentration by volume (e.g., ppmv and ppbv)
EPA	U.S. Environmental Protection Agency
GC/FID	Gas chromatography/flame ionization detector
GC/MS	Gas chromatography/mass spectrometry
GC/TCD	Gas chromatography/thermal conductivity detection
HASQAP	Hanford Analytical Services Quality Assurance Plan
HEPA	High-efficiency particulate air (filter)
HP	Hewlett Packard
IC	Ion chromatography
IL	Impact level (PNL quality assurance impact level)
IS	Internal standard
ISS	In-Situ Sampling System (used in FY 1994)
ISVS	In-Situ Vapor Sampling System (new, improved)
MDL	Minimum detection limit
NIST	National Institute for Standards and Technology
NPH	Normal parafin hydrocarbon
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
PBI	Performance-based initiative
PFA	Perfluoroalkoxy (Teflon™)
PNL	Pacific Northwest National Laboratory
ppbv, ppmv	Concentration by volume
QA	Quality Assurance
REL	Recommended exposure limit
RPD	Relative percentage difference
SCIC	Suppressed-conductivity ion chromatography
SIE	Selective ion electrode
SRM	Standard reference material
SUMMA™	Passivated stainless-steel whole-air collection vessel
STP	Standard temperature and pressure (0°C and 760 torr)
TEA	Triethanolamine
TCR	Tank characterization report
TIC	Tentatively identified compound
TNMHC	Total non-methane hydrocarbon compounds
TST	Triple sorbent trap (thermal desorption method)
TWINS	Tank Waste Information Network System
TWRS	Tank Waste Remediation System
UHP	Ultra-high purity
VSS	Vapor Sampling System (heated probe/truck)
WHC	Westinghouse Hanford Company



1.0 Introduction

Westinghouse Hanford Company (WHC) has the responsibility to report the characteristics of the headspace vapors of the radioactive waste tanks at Hanford. The Pacific Northwest National Laboratory (PNL) performed work in FY 1995 to support the characterization of headspace vapor in waste tanks at the Hanford Site. During the year, support for the PNL project shifted from the WHC Tank Waste Remediation System (TWRS) Safety Program to the WHC Characterization Program. The primary scope of the project in FY 1995 was to support analyses for organic vapor (SUMMA™ and sorbent trap/thermal desorption), permanent gas (SUMMA™), and inorganic vapor (solid-sorbent trains). The thermal desorption work scope was added to the PNL work scope during the second half of FY 1995. Tank headspace samples were obtained using the in-situ sampling system (ISS) and the vapor sampling system (VSS). In addition to the analytical activities; work scope in FY 1995 also included providing technical support for the vapor program, tank characterization report input, a tank vapor database, and other related activities.

This annual status report contains summarized information on work completed, progress and problems, and current status of the following tasks: management and technical support (Chapter 2.0), organic sampling and analyses (Chapter 3.0), inorganic sampling and analyses (Chapter 4.0), vapor data reports (Chapter 5.0), tank vapor database (Chapter 6.0), and conclusions and lessons learned (Chapter 7.0). Additional information is provided in the appendices. In the report, Hanford waste tanks are referred to in shortened form (e.g., tank 241-C-107 becomes C-107).



2.0 Project Management/Vapor Technical Support

Staff: MW Ligothke (Project Manager, June 1995 to present), SC Goheen (Project Manager, August 1993 to June 1995), JL Huckaby.

Project management objectives include planning and control of costs and schedules, on-time completion of deliverables, development and maintenance of a project work breakdown structure, implementation and oversight of quality assurance requirements, preparation of status reports, and preparation and reporting of budget and spending information. Additionally, the task included technical support for the WHC vapor project during the fourth quarter of FY 1995.

2.1 Summary of Work - FY 1995

Project staff supported the WHC tank vapor characterization project in FY 1995 by resolving a backlog of analyses and completing most data reports from sample jobs performed in FY 1994, by performing data analyses on samples from all 40 FY 1995 sample jobs, and by upgrading project quality assurance, instrumentation, and technical procedures. (The first sample job considered part of the FY 1995 PNL work scope was for waste tank C-107 on 9/29/94; the last was for T-110 on 8/31/95.) Of the 78 vapor sample jobs performed in FY 1994 and FY 1995 (involving 54 different tanks), reports were completed and issued for 27 by the end of FY 1995, reports for 35 others were completed and issued in October and November 1995, and the final 16 reports are scheduled to be issued in December 1995 and January 1996.

One WHC Key Milestone was required in FY 1995 and was completed on schedule (see below). Work also supported three additional milestones that are scheduled to be completed in FY 1996. Additionally, throughout the year project staff contributed to the successful completion of a Performance-Based Initiative (PBI) associated with the completion of Tank Characterization Report (TCR) input for vapor data from 42 sample jobs.

<u>Milestone</u>	<u>Type</u>	<u>Description</u>	<u>Completion</u>	<u>Status</u>
T2D-95-150	WHC Key	Complete vapor headspace sample analysis for all FeCN watch list tanks	4/28/95	Completed

Other contributions made by project staff, but not included elsewhere in this report, included a review of sample and analysis plans before sample jobs and participation in a vapor project conference in April 1995.

The level of Quality Assurance of work performed at PNL was upgraded during FY 1995 to PNL Impact Level II. This was largely accomplished during the first half of the year, with the exception of the thermal desorption method, which was added during the second half of the year. One result of this change was the preparation or improvement of formal technical procedures for all aspects of the analytical work performed. A list of these procedures is shown in Appendix A.

Accompanying the scheduled upgrades in the quality assurance level of the project in FY 1995 were two quality assurance assessments performed by WHC. The first, Assessment AR95-001, was performed in January 1995. Three observations and six concerns were identified by the assessment team, and after discussion, the PNL plan to resolve the comments was approved in July 1995. The resolution of issues from Assessment AR95-001 was formally accepted by WHC on 9/15/95. The second assessment, AR95-007, was performed in September 1995 to review the status of the new thermal desorption method implemented by PNL. Five observations and one concern were identified and followed in early October by a PNL plan to resolve the issues. Because resolution of these issues has been incorporated into the general second phase of quality

assurance upgrade (to meet the requirements of the Hanford Analytical Services Quality Assurance Plan [HASQAP, DOE/RL 1995]), it is expected that final formal resolution will be obtained after a planned early December audit of the project to HASQAP requirements.

Preparations were made for continuing tank headspace vapor characterization in FY 1996. Plans call for characterization of 30 tank headspaces and an additional 18 jobs aimed at resolving other issues (in-situ versus heated-probe sampling systems, sampling methodology, analytical methods, and spatial and temporal changes in vapor concentrations in selected tanks). Importantly, the requirement to perform analyses in accordance with HASQAP has been included in project authorizing documents, and that effort is expected to be completed during the first quarter of FY 1996. Additionally, the vapor project is expected to become more closely aligned with the other WHC Characterization Program activities; this move will change the way sample plans are generated, the way quality assurance is assessed, and how data reports are processed (formal clearance will no longer be required). Additionally, in FY 1996 it is expected that the full target-compound analyses (SUMMA™ TO-14 and thermal desorption) will be performed on selective samples rather than for every job.

2.2 Technical Support for Vapor Characterization

In January, WHC transferred to PNL the workscope and personnel to write waste tank headspace sampling and analysis summary reports. Previously, this task resided in the WHC Safety Program. The initial schedule for delivery of 25 reports by the end of May was changed, in March, to 33 reports to be delivered by the end of May. Eleven of the reports were cleared for public release in March and were distributed to members of the Tank Vapor Conference for review. The Tank Vapor Conference was convened in April, and the members indicated their general approval of the reports. The 33 reports were delivered to WHC as required, published as WHC reports, and given to DOE/RL to partially satisfy the requirements of a Performance Based Initiative (PBI). In addition, a summary of findings was written (with co-author Harry Babad of WHC), as a separate PBI deliverable.

DOE/RL comments on the 33 tank headspace characterization reports and the summary report were addressed in August and September. The summary report was revised and expanded to discuss various gas and vapor issues and to summarize the results from a total of 43 tanks. At the request of DOE/RL, nine additional tank characterization reports were written and delivered to DOE/RL by the end of September. The delivery of the 33 revised and nine new reports in September allowed WHC to essentially satisfy Safety Initiative SI-20 a month ahead of schedule.

Support was provided for the planned deployment of the ISVS sampling system. This support included the preparation of a draft plan for performing chamber tests of the HEPA and SUMMA™ sample line under realistic conditions. This work is planned to be completed in the first half of FY 1996. Also in FY 1995, a meteorological support activity was performed to provide information on conditions during vapor sample jobs and wind flow characteristics in the 241-C Tank Farm. The need for continued information with the shift to ISVS sampling is under consideration, and other continued support will be provided on a job-specific basis in FY 1996.

PNL supported WHC in all technical areas of the Vapor Program, including sample collection, analyses, and interpretation. Presentations on tank headspace mixing were given by PNL personnel to the Chemical Reactions Subpanel of the Tank Advisory Panel and to a combined meeting of this subpanel and the Defense Nuclear Facility Safety Board staff. PNL sent technical personnel to Westinghouse Savannah River, as requested, to help resolve tank headspace safety issues. Technical support for tank gas and vapor issues was provided on numerous occasions as requested by WHC TWRS Safety, Characterization, and Operations.

3.0 Organic Sampling and Analysis Task

Staff: JS Fruchter (Task Leader), BD McVeety, JC Evans, B Thomas, JL Julya, JA Edwards, TR Clauss, KB Olsen, GS Klinger, GA Ross, TL Almeida, TG Walker, and OP Bredt.

The objective of this task is to provide organic analyses for waste tank headspace samples at the Hanford site. Target organic analytes include the TO-14 analytes plus an additional 12 tank related compounds. The target analytes are detected and quantified in tank vapor samples collected in SUMMA™ canisters and/or vapor samples collected on triple sorbent traps. A variety of other volatile and semivolatile organic compounds are routinely identified in tank vapor samples by these two methods. SUMMA™ canister collected tank vapor samples are also analyzed under the TO-12 method to provide the total nonmethane hydrocarbon concentration. A suite of permanent gases, including hydrogen, nitrous oxide, methane, carbon dioxide and carbon monoxide are also analyzed in the tank vapor samples.

3.1 Sampling and Analytical Methods/Organic Task

3.1.1 Summary Staff supporting the organic task of the PNL tank vapor characterization project supported preparations for 45 tank vapor sample jobs plus a variety of other probe-cleaning and grab samples during FY 1995. All 45 of SUMMA™ canister sample sets were analyzed for permanent gases including hydrogen, carbon monoxide, carbon dioxide, nitrous oxide, and hydrogen. SUMMA™ canister samples from all 45 sample sets plus an additional 21 backlogged FY 1994 sample sets were analyzed for a target list of 53 compounds that included the 39 U.S. Environmental Protection Agency (EPA) TO-14 analytes plus an additional 14 tank-specific compounds. The method used was a modified TO-14 procedure (PNL-TVP-03). Fourteen of the samples were analyzed for total nonmethane hydrocarbons (TNMHC) using an adaptation of the EPA TO-12 method (PNL-TVP-08). In addition, 13 triple sorbent trap samples were analyzed using a thermal desorption method (PNL-TVP-10). The list of target compounds was extended to 62 compounds through the addition of several higher molecular weight alkanes and other tank-related compounds. This new target list was used on the tank sample jobs performed toward the end of FY 1995.

3.1.2 Technical Procedures The triple sorbent trap/thermal desorption analyses procedure, PNL-TVP-10, was prepared and approved. The method uses a DynaTherm thermal desorption unit coupled to a Hewlett-Packard 5972 gas chromatograph/mass spectrometer (GC/MS). Samples for the thermal desorption method, triple-sorbent traps (TST), from tanks A-101, AX-101, AX-102, and AX-103 were used to test the method. After development, a total of 13 tank headspace vapor samples were analyzed. The permanent gas analysis method, PNL-TVP-05, utilizing a Gas Chromatograph -Thermal Conductivity Detector was brought on line. A nitrogen carrier option was added to analyze for H₂ at increased sensitivity. Sensitivity testing was completed, and a total of 45 SUMMA™ canister samples were analyzed. A back-up permanent gas procedure, PNL-TVP-04, is being developed using a portable gas chromatograph with dual TCD detectors. An argon carrier and signal inverter was added to one detector channel to enhance H₂ sensitivity. A procedure for EPA TO-12 analysis, PNL-TVP-08, was also prepared and authorized. The TO-12 analysis method was put into operation beginning with the C-103 VMS samples obtained during July.

Procedures Improved: The TO-14 SUMMA™ canister analysis method, PNL-TVP-03, was revised to include use of the EnTech 7000 cryoconcentrators and to incorporate the TO-14 extended analytes analysis for tank headspace samples. In addition, it was determined that pressurizing SUMMA's before TO-14 analysis using the EnTech cryoconcentrator allowed for a

more consistent aliquot of sample to be pulled through the system for concentration, thus improving precision. The sample shipping and handling procedure, PNL-TVP-07, was revised to include the handling and tracking of the PNL triple-sorbent traps. Minor modifications were also made to the holding temperature requirements for the inorganic traps, and the sample delivery point.

3.1.3 Staff Training Two staff members traveled to Oak Ridge National Laboratory to discuss transferring TST sample collection and analysis methodology to PNL. A PNL TST capability was brought on line during FY 1995. Six staff members traveled to Orlando to complete training on the Thru-Put Systems Target software. The Target software is the basis for automated processing of vapor analysis data generated on instrumentation in the vapor analytical laboratory. Two staff members took Hewlett-Packard Gas Chromatography - Mass Spectroscopy training in September. The training emphasized the use of the EnviroQuant Chemstation. Other onsite training was accomplished to project quality assurance plans and technical procedures.

3.1.4 New Equipment and Software The GC/MS system and the thermal desorption system for the triple sorbent tube analysis was procured. The equipment was initially installed in the Sigma 5 Building for testing and method development. It was subsequently moved to the 326/23B laboratory for operational use. Work on repairing the second EnTech 7000 for use on the TO-12 analyses was completed. A new zero air generator installed in the 326 laboratory. The can cleaning operation was moved to the 329 laboratory. The atomic emission detector system was also moved to the 329 laboratory to provide space for the TST system in the 326 laboratory. A portable permanent gas instrument employing mini thermal conductivity detectors was purchased, installed and tested in the 326 laboratory. Fifty SUMMA™ canisters were purchased, bringing the total inventory to 270.

Computers and Software: The installation of the HP Chemserver was completed in early FY 1995. The full capability of the data processing software was realized after several custom programs were written. The system was fully implemented in early January, with all permanent gas and TO-14 analyses being processed through the Chemserver system. By May, work was completed on installing the network connection in the 326 laboratory and hooking up the UNIX data system to it. In the third quarter of FY 1995, a UNIX X-terminal and 4 gigabytes of additional disk storage was installed. Uninterruptable power supplies were added to each computer to filter out any abrupt power surges. A remote PC in the Sigma V building was configured to allow remote log in and Target/3 data reduction. This connection has been tested and the system is being utilized. The addition of the new X-terminal and multiple simultaneous users has caused significant performance problems on our Unix data system. We reached a point where we are overtaxing the main CPU system resource. A request was made and granted to upgrade the computer to a higher performance model. Purchase justification, and associated procurement paperwork was prepared, and the system was ordered before the end of FY 1995.

3.1.5 Sample Preparation and Control Sample preparation and control was provided for both types of organic task samples (SUMMA™ and thermal desorption).

SUMMA™ Canisters: Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified as contaminant-free according to PNL Technical Procedure PNL-TVP-02 (see Appendix 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 (see Appendix A), which is a modification of EPA compendium Method TO-14. If the canister is verified as clean and free of TO-14 and unknown contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if

any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 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.

Triple Sorbent Traps: Samples are collected on Supelco 300 graphite-based TST. Before field deployment, each trap is heated to 380°C under inert gas flow for a minimum of 60 min. Tubes are prepared in batches, with each tank sampling job constituting one batch. One tube is selected from each batch and run immediately to verify cleanliness. All remaining tubes in the batch receive equal amounts of three surrogate compounds (hexafluorobenzene, toluene- d_8 , and bromobenzene- d_5). One tube per batch is run immediately to verify successful addition of surrogate spikes to that batch. Tubes are then placed in individually labeled plastic shipping tubes (Supelco TD³), which are sealed with gasketed end caps, thus providing a rugged, headspace-free shipping and storage medium. As a precautionary measure, sample tubes are kept in refrigerated storage before and after sampling.

3.1.6 Sample Analyses Sample analyses were performed for permanent gases, total non-methane hydrocarbons, and volatile organic analytes (all from SUMMATM canisters) and for semi-volatile organic analytes (thermal desorption sorbent samples).

Permanent Gases: The SUMMATM canister samples were analyzed for permanent gases according to PNL Technical Procedure PNL-TVP-05 (see Appendix A) 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 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.

Standards for the permanent-gas analysis are blended from commercially prepared and certified standards for each of the analytes. The instrument is calibrated for CO , CO_2 , N_2O , and CH_4 over a range of 25 to 700 ppmv using standards at five different concentrations and He as a carrier gas. A similar procedure is followed for H_2 , except that the carrier gas was changed to N_2 . A least-squares linear-regression routine is applied to the calibration data set to generate the best-line fit for each compound.

Total NonMethane Hydrocarbons: The SUMMATM canister samples were analyzed according to PNL Technical Procedure PNL-TVP-08 (see Appendix A), which is similar to EPA compendium Method TO-12. The method detection limits in the sub mg/m^3 are required to determine total nonmethane hydrocarbon compounds (TNMHC) concentration in the tank samples.

The method uses an EnTech 7000 cryoconcentration system interfaced with a Hewlett-Packard 5890 gas chromatograph/flame ionization detector (GC/FID). The EnTech concentrator is used to pull a metered volume of 50 to 100 mL of sample air from the SUMMATM canister, which is 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) He. The purged TNMHCs are carried by a UHP He stream to the GC/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.

Twenty-four hours before the analysis, the SUMMA™ canister samples are pressurized with purified air (Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida). The starting pressure is first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level exactly twice the original pressure. For example, if the canister has a starting pressure of 740 torr, it is pressurized to 1480 torr. The sample dilution is taken into account when calculating the analysis results. The TNMHC result is calibrated using propane as the calibration standard and using that response factor as an external standard method. The instrument calibration mixture for the PNL-TVP-08 analysis consists of National Institute for Standards and Technology (NIST) 99.999% propane analyzed using a 5-point, multilevel, linear regression curve.

Before the tank samples are analyzed, a diagnostic check is 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. Second, an instrument continuing calibration verification is performed by analyzing 100-mL UHP propane and using the response factor as an external standard method, followed by one blank volume of Aadco air.

Volatile Organic Analytes: The SUMMA™ canister sample is analyzed according to PNL Technical Procedure PNL-TVP-03 (see Appendix A), which is a modified version of EPA compendium Method TO-14. The method uses EnTech 7000 cryoconcentration systems interfaced with a 5972 Hewlett-Packard benchtop 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, which has a 60-m by 0.32-mm internal diameter and 3-µm film thickness. The GC oven is programmed to run a temperature gradient beginning at 40°C, hold for 5 min, and ramp at 4°C per min to a final temperature of 260°C, with a 5-min hold. Twenty-four hours before the analysis, the SUMMA™ canister samples are pressurized with purified air (Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida). The starting pressure is first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level exactly twice the original pressure. For example, if the canister has a starting pressure of 740 torr, it is pressurized to 1480 torr. This dilution is an effort to improve the precision of the analysis. The sample dilution is taken into account when calculating the analysis results.

The instrument calibration mixture for the PNL-TVP-03 analysis consists of the standard 39 organic analytes with an additional 14 tank-related compounds. Together, these 53 compounds that are directly quantified in this analysis make up the target analyte list and are referred to as target analytes. The calibration mixture is prepared by blending a commercially prepared 39-compound TO-14 calibration mixture with a 14-compound mixture created using a Kin-Tek® permeation-tube standard generation system. The operation of the permeation-tube system follows the method detailed in PNL Technical Procedure PNL-TVP-06. The standard calibration mix is analyzed using four aliquot sizes ranging from 30 mL to 200 mL. A response factor for each compound was calculated. The GC/MS response for these compounds has been determined previously to be linearly related to concentration. 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 used.

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "high-sensitivity tune", as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated using a standard gas mixture containing 39 volatile organic compounds listed in EPA compendium Method TO-14 and an additional 14 tank-related compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d₅, and bromofluorobenzene was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, IS, and standards are obtained from the extracted ion plot from their selected mass ion. The calibration is generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank-headspace samples are analyzed.

Semi-Volatile Organic Analytes: The Supelco 300 tubes are analyzed according to PNL Technical Procedure PNL-TVP-10, with the exceptions noted in Section E.4 of that procedure. The method employs Supelco Carbotrap™ 300 traps for sample collection and preconcentration. The traps are ground-glass tubes (11.5 cm long x 6 mm OD; 4 mm ID) containing a series of sorbents arranged in order of increasing retentivity. Each trap contains 300 mg of Carbotrap™ C, 200 mg of Carbotrap™ B, and 125 mg of Carbosieve™ S-III. The first two sorbents are deactivated graphite with limited sorption power for less volatile compounds. The final trapping stage, the Carbosieve™ S-III, is a graphitized molecular sieve used to retain the most volatile components, including some permanent gases such as Freon-12. Following sample collection and addition of IS, the traps are transferred to a Dynatherm ACEM 900 thermal desorber unit for analysis. The trap on the ACEM 900 is then desorbed by ballistic heating to 350°C and the sample is then transferred to a smaller focusing trap. A10:1 split is used during the transfer with 10% of the sample analyzed and the rest retained for reanalysis. The split sample collected on a second identical Carbotrap™ 300 trap is used for repeat analysis on at least one sample per batch. Since the IS also follows the same path, quantitation may be performed directly on the repeat run without changing the calibration. Following desorption from the Carbotrap™ 300 trap, the analyte is transferred to a long, thin focusing trap filled with the same type of trapping materials as the Carbotrap™ 300 traps and in approximately the same ratios. The purpose of the focusing trap is to provide an interface to a capillary GC column, which may be thermally desorbed at a helium flow rate compatible with the column and mass spectrometry interface (1.2 mL/min). The focusing trap is ballistically heated to thermally desorb components onto a capillary GC column. The column is subsequently temperature programmed to separate the method analytes, which are then detected by mass spectrometry.

The instrument calibration mixture for the TST analysis consists of the standard 37 organic analytes with an additional 14 tank-related compounds. Two compounds typically found on the TO-14 list are not included--bromomethane and benzyl chloride. Together, these 52 compounds that are directly quantified in this analysis make up the target analyte list (these 52 compounds will be referred to as target analytes). The calibration mixture is prepared in common with the mixture used for the SUMMA™ analysis. The standard calibration mix was analyzed using four aliquot sizes ranging from 100 mL to 1200 mL, and a response factor for each compound was calculated. Volumes of standard added to the traps are measured by pressure difference on a SUMMA™ canister of known volume. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. 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 used.

Before the tank sample is analyzed, a diagnostic check was performed on the GC/MS instrument by running a full auto tune, as described in PNL-TVP-10. Upon satisfactory completion of the instrument diagnostic check, a blank tube was analyzed to check the cleanliness of the system. The instrument was then calibrated using a 300-mL volume of standard gas mixture containing 52 compounds. A gas mixture containing difluorobenzene, chlorobenzene-d₅, and 1,4-bromofluorobenzene was used as an IS for all calibration standard and sample analyses. Analyte responses from sample components, IS, and standards are obtained from the extracted ion plot from their selected mass ion. A continuing calibration is generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample.

3.1.7 Sample Calculations and Reviews Sample calculations and reviews were performed for permanent gases, total nonmethane hydrocarbons, and volatile organic analytes (all from SUMMA™ canisters) and for semi-volatile organic analytes (thermal desorption sorbent samples).

Permanent Gases: Each analyte was quantitated by direct comparison of sample analyte peaks to the calibration plot generated for the compound. The lowest calibration standard for each analyte is reported as the method detection limit. 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 generally falls within ± 25% of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. An N₂ reagent blank, an ambient-air sample collected ~ 10 m upwind of tank being sampled, and the ambient air collected through the VSS were used as method blanks and to determine the potential for analyte interferences in the samples.

Volatile Organic Analytes: The quantitative-analysis results for the target analytes were calculated using the average response factors generated using the IS method described above and in PNL-TVP-03. The conversion from ppbv to mg/m³ assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

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

The concentration of each TIC is 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/m³:

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

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/m³ and the molecular weight of the analyte.

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

The IS level added to all blank, standard, and sample injections was 104 ppbv for bromochloromethane, 101 ppbv for 1,4-difluorobenzene, 98.5 ppbv for chlorobenzene-d₅, and 104 ppbv for bromofluorobenzene. The IS concentrations are converted from ppbv to mg/m³ at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, 117.6 for chlorobenzene-d₅, and 175.00 for bromofluorobenzene. All calculated sample concentrations were multiplied by a factor of two to account for a dilution step.

Semi-Volatile Organic Analytes: The quantitative-analysis results for the target analytes were calculated directly from the calibration curve generated using the IS method described above and in PNL-TVP-10. It should be noted that the relative response factor value for tetrachloroethylene, 1-2-dibromoethane, and toluene were calculated using the first IS, not the second IS, which is nearest in retention time to these compounds. The second IS is used to calculate the relative response factor for these compounds for subsequent analyses. The conversion from ppbv to mg/m³ assumes STP conditions of 760 torr and 273K and was calculated directly from the following equation:

$$\text{mg/m}^3 = \frac{(\text{ppbv}/1000) \times \text{g mol wt of compound}}{22.4 \text{ L/mol}} \quad (3.4)$$

The TICs are determined by mass-spectral interpretation and comparison of the spectra with the EPA/NIST and WILEY libraries, which are a part of the Hewlett-Packard 5971/5972 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one-tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. The quality of the mass-spectral searches was reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

The concentration of each TIC is estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area is used to calculate a response factor using the IS concentration in mg/m³:

$$\text{Response Factor} = \frac{\text{IS conc. (mg/m}^3\text{)}}{\text{IS peak area}} \quad (3.5)$$

The calculated response factor is then multiplied by the TIC peak area to give an estimated concentration for that compound. The ppbv concentrations are calculated from mg/m³ and the molecular weight of the analyte.

$$\text{TIC in ppbv} = \frac{\text{TIC (mg/m}^3\text{)} \times 22.4 \text{ L/mol} \times 1000}{\text{TIC g mol wt}} \quad (3.6)$$

The IS concentrations are converted from ppbv to mg/m³ at STP using a molecular weight of 114.09 for 1,4-difluorobenzene, 117.6 for chlorobenzene-d₅, and 174.0 for 1,4-bromofluorobenzene.

3.1.8 Data Reports and Technical Papers Data packages were prepared for the analyses of 54 VSS and ISS tank headspace samples, including the backlogged FY 1994 tanks. The organic portion of the final data reports was prepared for 49 of the tank sample sets. Data packages and reports were submitted on time to meet the WHC PBI.

A manuscript and a poster titled "Identification and Measurement of Permanent Gases and Volatile Organic Compounds in Hanford Waste Tank Headspace" was prepared and submitted to the Waste Management 95 Conference in Tucson. A PNL staff member traveled to Tucson to give the poster session. The manuscript was published in the meeting proceedings. An abstract titled "Vapor Characterization of Hanford Waste Tanks using SUMMA™ Canisters and GC/MS Analysis" was prepared for the 43rd ASMS Conference on Mass Spectrometry and Allied Topics in Atlanta. A poster was presented and an extended abstract was published in the meeting proceedings. An abstract titled "Vapor Characterization of Hanford Waste Tanks Using SUMMA™ Canisters and GC/MS analysis" was prepared and submitted to the ACS Northwest Regional Meeting in Park City. A presentation was given and an abstract was published in the meeting proceedings. An abstract was prepared and submitted to the ORNL-DOE conference on Analytical Chemistry titled "Performance Comparison Between SUMMA™ Canister and Triple Sorbent Tube Sampling and Analysis Methods as Applied to the Hanford Waste Tank Vapor Characterization Program."

3.2 Method Validation and Special Studies/Organic Task

After a preliminary report of the presence of methylisocyanate in triple-sorbent trap samples was made by Oak Ridge National Laboratory (ORNL), investigators at PNL developed methods for the potential analysis of methylisocyanate were investigated. Six SUMMA™ canisters were spiked with methylisocyanate and analyzed. Methylisocyanate was recovered from the spiked canisters that contained pure nitrogen, but none was recovered from the canisters containing tank vapors.

Input concerning organic vapor results from tank headspace samples was provided to the Vapor Conference Committee meeting in April 1995.

A limited comparison study between the TST and SUMMA™ canisters methods was run on two sets of tank samples. The C-103 blower samples and the A-101 VSS samples were chosen for investigation because they exhibited the most complex matrix of all samples obtained recently. TST traps were loaded from the SUMMA™ canisters, and the both the TST and SUMMA™ canisters were analyzed. The target compound quantities were compared and found to agree within $\pm 10\%$ of each other for the list of target compounds found. While the initial results are positive, this study has the following limitations:

1. only two tanks were compared providing a limited representation of all the organic compounds present in the 177 Hanford waste tanks
2. only target compounds were compared which are the compounds with which each method is specifically calibrated. The quantitation of TICs is more complicated as it depends specifically on the response factor for the nearest eluting internal standard and the delivery efficiency of a specific analyte through the concentration and separation hardware. The calibration process for a target compound accounts for some of this variability.

Several special heating mantles made to fit the SUMMA™ canisters were ordered. Temperature controllers were built to regulate precisely the temperature of the SUMMA™ canisters during analysis. The issue of heating versus not heating the canisters during analysis has not been given a detailed review, but from the limited studies done using our TO-12 analysis methods there

does not appear to be a discernible effect. We looked at several archived canisters collected from several tanks in the C and BY farms, which were specifically chosen because they contained significant quantities of normal paraffin hydrocarbon (NPH) compounds, assuming that those samples would show the greatest change from heating. We found that the TO-12 derived nonmethane hydrocarbon concentrations were essentially unchanged in canisters heated to 130°C. This study is by no means exhaustive, and the results can be extrapolated to the TO-14 analysis by analogy only. The study does indicate that the heating versus not heating issue is probably not as important as other issues.

3.3 Quality Assurance/Organic Task

The laboratory portion of the WHC QA audit AR95-001 was completed. All observations were successfully resolved and closed out. The laboratory portion of the WHC QA audit AR95-007 was completed. A corrective action plan to respond to the observations and concerns was developed, and implementation of the some of the corrective actions was initiated. The remaining corrective actions will be completed in FY 1996.

A precision and accuracy study and a method detection limit study were completed for the TO-14 SUMMA™ method.

A data checking step for all analyses in the organic vapor characterization task was instituted.

The TO-14 standards prepared by two different commercial companies were compared to assess relative performance. The two standards compared well for most of the compounds, but there were significant differences (> 35%) between the instrument responses for a few of the compounds. A standard is being procured from a third, independent supplier, which will provide a more complete data set for further analysis.

Preparations for instituting HASQAP standards for the organic vapor characterization task were implemented.

3.4 Accomplishments/Organic Task

Laboratory-support activities were, in general, completed on schedule. Backlogged analyses and reports from FY 1994 vapor jobs were largely completed. Sample analyses from FY 1995 jobs were completed by the end of the fiscal year, with the exception of jobs performed in August 1995. Specific laboratory-support activities included the following:

1. Prepare procedure for permanent gas analysis by mass spectroscopy. Changed to developing permanent gas method on new GC system (completed on schedule 8/31/95).
2. Perform laboratory operations and maintenance (9/29/95).
3. Complete tank reports for samples received late in FY 1994 (6/30/95).
4. Complete vapor headspace sample analysis for watch list tanks (6/15/95).
5. Procure HP 5972 GC/MS with Graseby NuTech concentrator (3/24/95).
6. Procure thermal desorption system (6/15/95).
7. Procure portable permanent gas system (6/15/95).
8. Procure SUMMA™ canister cleaning station (6/15/95).
9. Procure sorbent-tube expansion module for thermal desorption system (currently

unfunded).

10. Procure UNIX system terminal (7/31/95).
11. Procure UNIX workstation upgrade (9/29/95).
12. Procure TO-14 standard from Air Liquide for comparison with Scott and Matheson supplied gases (9/29/95).

3.5 Major Problem Areas and Resolution/Organic Task

The QA assessment of the PNL vapor project (AR95-001) resulted in one observation involving the organic task. This observation was resolved by conducting a method detection limit study and a precision and accuracy study.

The QA assessment of the triple-sorbent trap procedure held in September (AR95-007) resulted in five observations and one concern. As a result, PNL developed an action plan that detailed the laboratory's responses to the observations. These responses are being combined with the organic vapor laboratory's plan for implementing HASQAP requirements. It is expected that full compliance with HASQAP and reconciliation of the audit observations will be achieved by November 30, 1995.

4.0 Inorganic Sampling and Analysis Task

Staff: MW Ligothke (Task Leader), KH Pool, SO Slate, L Thomas, GW Dennis, and KP Schielke.

The objective of the inorganic task was to provide technical support and inorganic analytical chemistry for waste tank headspace samples. Support was provided for vapor sampling system (VSS) operations. Inorganic components from tank vapor samples were analyzed. Available analyses included those for ammonia, nitrogen oxides, sulfur oxides, hydrogen cyanide, and water from the vapor spaces of various waste tanks located at the Hanford Site.

4.1 Sampling and Analytical Methods/Inorganic Task

4.1.1 Summary Staff supporting the inorganic task of the PNL tank vapor characterization project supported preparations for all 40 VSS vapor sample jobs scheduled in FY 1995, analyzed sorbent trap data from 38 jobs, and completed 38 report chapters. The work to analyze and provide data report input for the remaining two jobs was completed on schedule in October 1995. Support was also provided for the effort to complete late-FY1994 sample jobs and resolve the backlog of reports from sample jobs performed in FY 1994; report input was provided for 19 such sample jobs. In FY 1995, samples were provided and analyzed for ammonia, nitrogen dioxide, nitric oxide, and vapor mass (largely water). Samples for hydrogen cyanide and sulfur oxides were not included in sampling and analysis plans for any vapor jobs performed in FY 1995.

4.1.2 Technical Procedures As part of upgrading to PNL QA Impact Level II, the procedure PNL-TVP-07 was prepared and implemented in October 1994. This procedure guides sample selection, preparation, control, analyses, and calculation of results for selected inorganic analytes. Used as the overall procedure for the inorganic task, the procedure contains references to other PNL analytical methods and quality assurance documents.

4.1.3 Staff Training One PNL staff member traveled to Lachat Instruments in Milwaukee to complete training on the use of the flow-injection system for analysis of ammonia samples. Other on-site training was accomplished to project quality assurance plans and technical procedures.

4.1.4 New Equipment and Software A Lachat Instruments Quick-Chem 8000 system was obtained to improve the efficiency of ammonia analyses. No new computer equipment or software was obtained.

4.1.5 Sample Preparation and Control Samples were prepared and controlled as per technical procedures PNL-TVP-07 and PNL-TVP-09. Samples consisted of glass tubes containing sorbent media were connected in series using PFA Teflon® tubing. Once prepared, samples were controlled using a chain-of-custody form and provided to WHC for use in sampling tank headspaces. On the return of the samples, the sorbent trains were disassembled and processed. The order of the sorbent trains used, from upstream to downstream end, was typically $\text{NH}_3 + \text{NO}_x + \text{oxidizer} + \text{NO}_x + \text{H}_2\text{O}$. In the trains, NO_2 was collected in the first NO_x trap and then NO was converted to NO_2 in the oxidizer section and subsequently collected in the second NO_x trap. To test the influence of the NH_3 trap on the collection of NO_x (NO_2 and NO), some sample and analysis plans called for alternate sorbent trains; these usually consisted of $\text{NH}_3 + \text{H}_2\text{O} + \text{H}_2\text{O}$ or $\text{NO}_x + \text{oxidizer} + \text{NO}_x + \text{H}_2\text{O}$. Trip and/or field blanks sorbent trains were provided with samples for each job. To test recovery, blank and samples were spiked with known quantities of analytes during selected jobs in FY 1994, and similar work is also planned in FY 1996. The two-section sorbent traps used for vapor sampling included: 500 mg + 250 mg carbon

beads impregnated with sulfuric acid (NH₃), 400 mg + 200 mg of a zeolite impregnated with triethanolamine (NO₂ and NO), and 300 mg + 150 mg silica gel (water). Additional information on sample preparation and control is provided in the body of data reports for each job.

4.1.6 Sample Analyses All sample analyses were performed following the technical procedure PNL-TVP-09. After disassembly of the sorbent trains, the individual segments were weighed to provide information on the mass change of the overall sorbent train which provided information on the total mass concentration of water in the tank headspace. Interference from other vapor mass (e.g., organics) was not significant. The sorbent traps used to collect NH₃, NO₂, and NO were then individually disassembled and analyzed by primary "front" and secondary "back" sections. In general, sorbent media from the samples were contacted with aqueous solutions to desorb collected analytes; specific details of the analyses are described in the data reports. Because of consistent results, and because in the case of NO₂ and NO the sorbent media contained significant levels of analyte, sample results were typically corrected for trip or field blanks. The specific nature of any corrections was identified in the specific data reports. Methods were confirmed previously using spiked blanks and samples (Clauss et al. 1994, Ligoetke et al. 1994).

4.1.7 Sample Calculations and Reviews The analytical results were used, along with sampling information provided by WHC (sample rates, durations, volumes, etc.), to calculate headspace vapor concentrations. 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 0°C and 760 torr), in L, by 22.4 L/mol. For example, the concentration (C_v) of a 3.00-L sample containing 75.0 μg of NH₃ equals

$$C_v = \frac{75.0 \mu\text{g}}{17.0 \text{ g/mol}} \times \left| \frac{3.00 \text{ L}}{22.4 \text{ L/mol}} \right|^{-1} = 32.9 \text{ ppmv.} \quad (4.1)$$

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.

After completing initial calculations, results were confirmed by a second individual before final input was provided for the data reports. Original and confirming work was documented.

4.1.8 Data Reports and Technical Papers Staff contributed to two new data reporting templates, providing information on samples, techniques, analyses, quality assurance, results, quality control, and summaries. Input was provided for 38 of 40 FY 1995 sample jobs and for 19 FY 1994 sample jobs. Staff also contributed to a few technical abstracts for conferences and project reviews.

4.2 Method Validation and Special Studies/Inorganic Task

Method validation work performed to test methods used by the inorganic task to date have included samples and controls used in selected vapor sample jobs performed in FY 1994 and a hold-time study performed in FY 1995. A summary of the results of the FY 1994 measurements, previously described in other reports, and a detailed description of the results of the FY 1995 hold-

time study are provided in Appendix B. Results of both studies indicated no apparent trends in the accurate recovery of analytes from the sorbent media with the potential exception of very small quantities of nitrite.

4.3 Quality Assurance/Inorganic Task

Analytical work was performed according to quality levels identified in the project QA plan and several PNL documents. The samples were analyzed following PNL Impact Level II. The PNL documents include PNL-MA-70 (Part 2), PNL-ALO-212, PNL-ALO-226, and MCS-046. A summary of the analysis procedures and limits for the target inorganic compounds is provided in the table (below). The table also shows generic expected and 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 object assessment by Osborne et al. (1994). The table shows 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 with a vapor-sample volume of 3 L and a desorption-solution volume of 3 mL (10 mL for NH₃).

The accuracy of concentration measurements depends on potential errors associated with both sampling and analysis. Sampling information, including sample volumes, was provided by WHC; sample volume uncertainty was not provided. The uncertainty of analytical results, which depend on the method used, was estimated to be within allowable tolerances (Osborne et al. 1995). For NH₃ analyses, the accuracy of laboratory measurements by selective ion electrode (SIE) was estimated to be $\pm 5\%$ relative, independent of concentration at 1 $\mu\text{g}/\text{mL}$ 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-traceable standard reference material (SRM) by using an independent calibration verification standard, which is certified to be NIST-traceable. Nitrite analyses (for NO₂ and NO)

Table Analytical Procedures, Detection Limits, and Expected and Notification Levels for Selected Inorganic Analytes. Analytical precision and accuracy targets for results in the expected ranges equal $\pm 25\%$ and 70 - 130%, respectively. (Osborne et al. 1994).

Analyte	Formula	Procedure	MDL ^(a)		Expected Range ^(b) (ppmv)	Notification Level ^(b) (ppmv)
			(μg)	(ppmv)		
Ammonia	NH ₃	PNL-ALO-226	0.1	0.5	≥ 2	≥ 150
Nitrogen dioxide	NO ₂	PNL-ALO-212	0.02	0.02	≥ 0.1	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.02	0.02	≥ 2	≥ 50
Mass (water) ^(c)	n/a	PNL-TVP-09	0.6 mg	0.2 mg/L	$\geq 3 \text{ mg/L}$	n/a

- (a) 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 may be obtainable. Determination of the MDLs was also based on desorbing-solution volumes of 10 mL for NH₃ and 3 mL for NO and NO₂. The MDL for water was based on the typical variation in mass change of 5-trap field-blank sorbent trains that accompany samples to the field.
- (b) As per Table 7-1 in Osborne et al. (1994). Notification levels require verbal and written reports to WHC on completion of preliminary analyses.
- (c) The vapor mass concentration, thought to be largely water vapor, is determined for estimates of headspace humidity.

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 NH₃ above, the estimated maximum bias for samples derived from sampling for NO₂ is $\pm 10\%$, and for samples derived from sampling for NO, it is $\pm 5\%$ relative. The accuracy of measurements of sample mass is typically ± 0.1 mg, or less than 1% of the mass changes of typical 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 less than ± 1 mg per 5-trap sorbent train.

4.4 Accomplishments/Inorganic Task

Laboratory-support activities were, in general, completed on schedule. No sample sets were backlogged, and the backlog of report input from FY 1994 was resolved. Sample analyses from FY 1995 vapor jobs were completed by the end of September, and report input for all jobs was provided by early October, as scheduled. Other activities accomplished in FY 1995 included the following:

1. Procurements were made, and the required analytical capabilities were maintained throughout the year (completed on schedule on 9/29/95).
2. A technical procedure was prepared for inorganic analyses (10/17/94). The procedure was revised in April 1995.
3. A new analytical system was procured to aid analysis of ammonia samples (6/28/95).
4. All report input was completed for FY 1994 sample jobs (1/31/95).
5. All analyses were completed for FY 1995 samples (9/15/95). All report input was completed for FY 1995 sample jobs (completed 10/14/95).
6. Input was completed for the year-end status report (completed 10/31/95).

4.5 Major Problem Areas and Resolution/Inorganic Task

No major problems were encountered in FY 1995. The QA assessment of the vapor project (AR95-001) resulted in one observation involving the inorganic task. The task-level technical procedure was revised in April to address the observation.

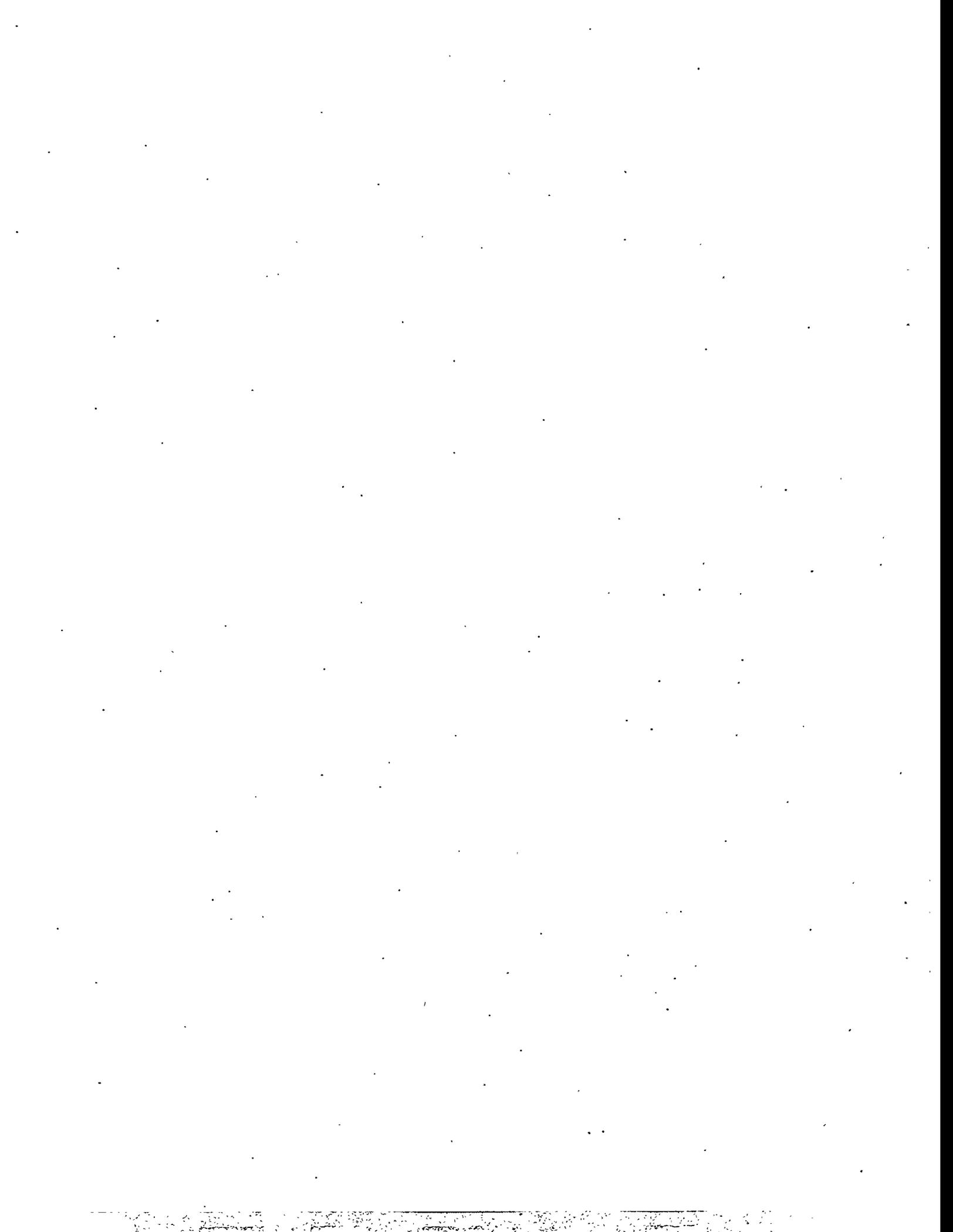
5.0 Waste Tank Vapor Data Reports

Staff: KL Silvers (Task Leader), OP Bredt, BM Thornton, M McCulloch, and WC Cosby.

The analytical results of samples from the headspaces of waste tanks were reported for jobs performed in FY 1994 and FY 1995. In FY 1994 and early FY 1995, five reports were issued from samples obtained during several sample jobs in Tank C-103. In FY 1995, 22 reports were issued of data from 13 VSS and 9 ISS vapor sample jobs. Work was also completed on an additional 35 reports (29 VSS and 6 ISS). After this set of reports is released, four reports from ISS jobs in FY 1994 and 11 reports from VSS jobs late in FY 1995 will remain to be completed. A current list of data reports is shown in Appendix C. In summary, of 77 vapor sample jobs performed in FY 1994 and FY 1995^(a), reports were completed and issued for 27 by the end of FY 1995, reports for 35 others were completed and issued in October and November 1995, and the final 15 reports are scheduled to be issued in December 1995 and January 1996.

Report format changes were made twice during the year based on the addition of new analyses and review comments from WHC and DOE/RL. Another minor revision is planned early in FY 1996 as the requirement to publish the reports has been relaxed; the analytical results will be issued as letter-format reports to be consistent with other data-generating activities supporting the WHC Characterization Program. The first report using the newest format will be that for TX-111 (sampled on 10/12/95); the report is scheduled to be issued in December 1995.

(a) Of the 78 vapor sample jobs, 54 different tanks were sampled. One tank (C-103) was sampled five times during the initial development phase of the tank vapor characterization project. Twenty other tanks have each been sampled twice, once each using the VSS and ISS sampling methods. Samples from four other tanks have been analyzed under the support of other projects and are not included in the totals above (AN-107, C-103 VMS, C-301 IMUST, and SX-104 LOW).



6.0 Waste Tank Vapor Database

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Information in the Tank Vapor Database is being used to characterize the waste in the tanks and to help make decisions on worker safety issues. The objectives of the Tank Vapor Database task in FY1995 were to load published data about the vapor phase of the waste in single-shell tanks at the Hanford Site, increase the accessibility of the data, and expand the ease of use of the Tank Vapor Database. These objectives were successfully met in FY 1995, with plans for future enhancements in FY 1996.

6.1 Introduction/Vapor Database

The purpose of the database is to store sample data from the tanks, analysis results from the laboratories, and chemical properties of the constituents found. The database will be used to aid in characterizing the waste in the tanks and to help make decisions on worker safety issues.

6.1.1 History of Tank Vapor Database In 1993, WHC directed PNL to develop extensive database capabilities to support the vapor characterization effort. The system, set in a client/server environment with a Sybase engine and using DataPrism as an initial query tool, was implemented by the end of FY 1994. In FY 1995, significant quantities of data have been loaded and validated into the database and other significant tasks have been accomplished.

6.1.2 The Place of the Tank Vapor Database at Hanford The Tank Vapor Database fits into the larger picture of information management in two ways: through the Tank Waste Information Network System (TWINS) and as a separate database. TWINS provides a standardized database format and an integrated graphical user interface that allows access to a vast array of data on the solid, liquid, and vapor phases of waste stored at various locations in the DOE complex. The data that are accessible through TWINS are actually stored on separate databases: two of these databases are the Tank Characterization Database and the Tank Vapor Database. The Tank Characterization Database contains the solid and liquid data from the Hanford Site tanks. TWINS provides a convenient interface in allowing the user to see both sets of data without having to learn the different data structures. The Tank Vapor Database can also be used as a stand-alone database and accessed through commercial front-end software such as DataPrism.

6.1.3 Tank Vapor Database Registered Trademarks.

Access Microsoft Corporation, Redmond, Washington.

DataPrism Brio Technology, Mountain View, California.

Excel Microsoft Corporation, Redmond, Washington.

Sybase Sybase, Inc., Emeryville, California.

Lotus 1-2-3 Lotus Development Corporation, Cambridge, Massachusetts.

Visual Basic Microsoft Corporation, Redmond, Washington.

6.2 Summary/Vapor Database

Data were loaded from 33 tanks during FY 1995. A number of methods were used to significantly improve the data loading. These methods included designing several programs in Visual Basic. Also, a program was written to assist in validating the data. The context of the data (such as detailed information about the methods used) was made more accessible by loading the complete reference citation for the published reports. To improve the efficiency of processing the chemical data, unique identifiers were created for less well-defined chemicals and mixtures. To

improve the query speed and to capture the data sent from the other laboratories to PNL, the data model was revised.

A decision was made to use the Tank Waste Information System (TWINS) because the system could easily make the data accessible to a wide number of users (as described in Section 6.1.2). To integrate the Tank Vapor Database into TWINS, the team worked with the TWINS staff to fit the database seamlessly into the overall structure of TWINS and organize the data logically for vapor users.

Several upgrades were made to the system this fiscal year. The database was moved to a substantially better server, a Sparc1000. Also, the operating system and database engine were upgraded.

6.3 Loaded Vapor Data

Progress was made to enhance the loading of vapor information, referencing data, identifying Chemical Abstract Services (CAS) numbers, and categorizing chemical constituents.

6.3.1 Sampling, Analytical, and Chemical Data Loading Partially Automated This fiscal year, vapor sampling data for 33 tanks were loaded (as of 8/1/95) from published reports into the Tank Vapor Database and validated (Appendix D). Where possible, the information in the reports was sent to the Tank Vapor Database team in Excel or Lotus 1-2-3 spreadsheets, which reduced the possibility of data entry errors.

Data loading from the electronic spreadsheets was significantly improved by a number of methods. One way the data loading was improved was by creating a Visual Basic program that reformatted the laboratories spreadsheets so they could be easily loaded. To effectively load chemical information, the Tank Vapor Database team consulted with the Hanford Technical Library staff. Through discussion with the library staff, an innovative way was found to accurately load the CAS number and other chemical information from an ASCII file sent by the library.

To assist in validating the data, a program was designed to check the CAS numbers and names provided by the laboratories against a list provided by the Hanford Technical Library. The result is two lists, one that contains valid names and CAS numbers and one that contains invalid names and numbers. This information is then checked with the appropriate laboratory staff and corrections are made as necessary.

6.3.2 Reference Data Provided Access to Contextual Information To provide the user with the context of the data (such as the laboratory reports and gas chromatograph runs), the complete reference citation was stored for the reports that contained the data loaded into the database. The information was entered through a user-friendly input screen created in Access. New concerns about the public availability of the vapor documents were resolved through several discussions with the Clearance Office.

6.3.3 CAS Numbers Created for Data Integrity When analyzing the tank vapor samples, the laboratories occasionally listed chemicals that did not have CAS numbers. The CAS number is critical to the data loading process because it provides a unique, easily recognizable code for each chemical. However, not all of the chemicals identified in the tanks are well defined and, therefore, have not been assigned CAS numbers. For example, C₄-alkane could be butane or methylpropane; in heptanol, the position of the alcohol group is ambiguous. Also, CAS numbers are not assigned to combinations of chemicals (for example, butane and other alkanes). So, to load the chemical data into the database substitute unique identifiers were needed for these generic chemicals (such as C₄-alkane, heptanol) and combinations of chemicals. This unique identifier

system is being created using a systematic approach that can be replicated by others who need to add data to the Tank Vapor Database (Appendix D).

6.3.4 Chemical Categorization Included for Easier Group Analyses To assist users in looking at the chemicals contained in the vapor phase of the tanks, a new data field was added containing the component type (such as alkanes, alkenes) to which the chemical constituent belonged. This information was pulled from a variety of reference sources and entered using an Excel and Visual Basic program, which helped to automate the data loading process.

6.4 Improved Data Accessibility

Data accessibility was improved by working with TWINS staff, upgrading system hardware and software, and revising the structure of the data model.

6.4.1 Working with TWINS Staff Because TWINS is the pathway for making the data accessible to a wide number of users, the vapor data needed to fit seamlessly into the overall structure of TWINS and to be organized logically for vapor users. To allow the user to choose the desired data quickly from the list of tables, definitions of the types of data in the tables were provided. This information was found in the data catalog. The data catalog contains detailed information on each subject area, such as the category of table, column titles, type and length of each field, whether or not fields are queriable, and the look-up options. The data catalog was populated using an online tool developed in Access, which saved time on loading and modifying the information into TWINS, with information from the data dictionary. The data dictionary defines the tables and fields.

The team helped ensure that all potential users of the vapor data were aware that they could access it through TWINS. The team also facilitated in getting accounts for the users who requested them. User support was provided on several occasions by the Tank Vapor Database team. This included traveling to the user's location, setting up the connections for TWINS and DataPrism, providing the user with general notes on accessing the vapor data, and helping the user retrieve the data on a sample query. The majority of the training was done by the TWINS staff because most users access the data using TWINS. This policy conforms to the basic philosophy of both TWINS and the Tank Vapor Database.

When the TWINS staff made the development version of the new enhancements to the interface available, the Tank Vapor Database team reviewed the changes and the impact on the vapor data. Input was provided to the TWINS team that enhanced the communications aspects of the interface, and modifications were made to accommodate these changes.

6.4.2 Migrated to Sparc1000 Server In FY 1994, the Tank Vapor Database team purchased the Sparc1000 server labeled "Pygar." In FY 1995, the vapor database was moved to the new server; this involved three basic changes. First, the server was significantly upgraded from a Sparc2 to a Sparc1000. Second, the operating system has been upgraded from Sun O/S to Solaris 2.4. Third, the database engine was upgraded from Sybase 4.9.2 to Sybase 10.0.2.1. This move to the new server allows the user to retrieve and manipulate data faster. It also allows the database administrator to perform administrative functions faster and more efficiently. An enhanced schedule of data backups improves the reliability of the data. Because more disk space is available, the data structure has been optimized for both update and retrieval. These systems are "cutting edge" technology and will be supported by both in-house computer support and the suppliers for some time.

6.4.3 Revisions to the Database Model The structure of the data model was revised to reflect the information that was provided by the laboratories and to make it more useful in the long term (Appendix D). In FY 1994, several pieces of information were assumed to be

provided by the analytical laboratory. The data were not collected or not readily discernible when the analyses were performed; thus, these fields, which included analytical procedures and number of analyses, were deleted. The distinction between laboratory and company was determined to be artificial and was deleted. The toxicology data were deleted as well. On the other hand, after discussions with the users, additional information was captured by the database. Tentatively identified compounds, nonstandard unit conversion information, and the categorization of chemicals were included. Also, the concept of below detection limit was significantly expanded. These changes made the database more accurately reflect the information stored in the reports and enhanced its usefulness in the future.

6.5 Future Plans for the Tank Vapor Database

The coming fiscal year brings numerous possibilities for additional enhancements to the Tank Vapor Database, including the following:

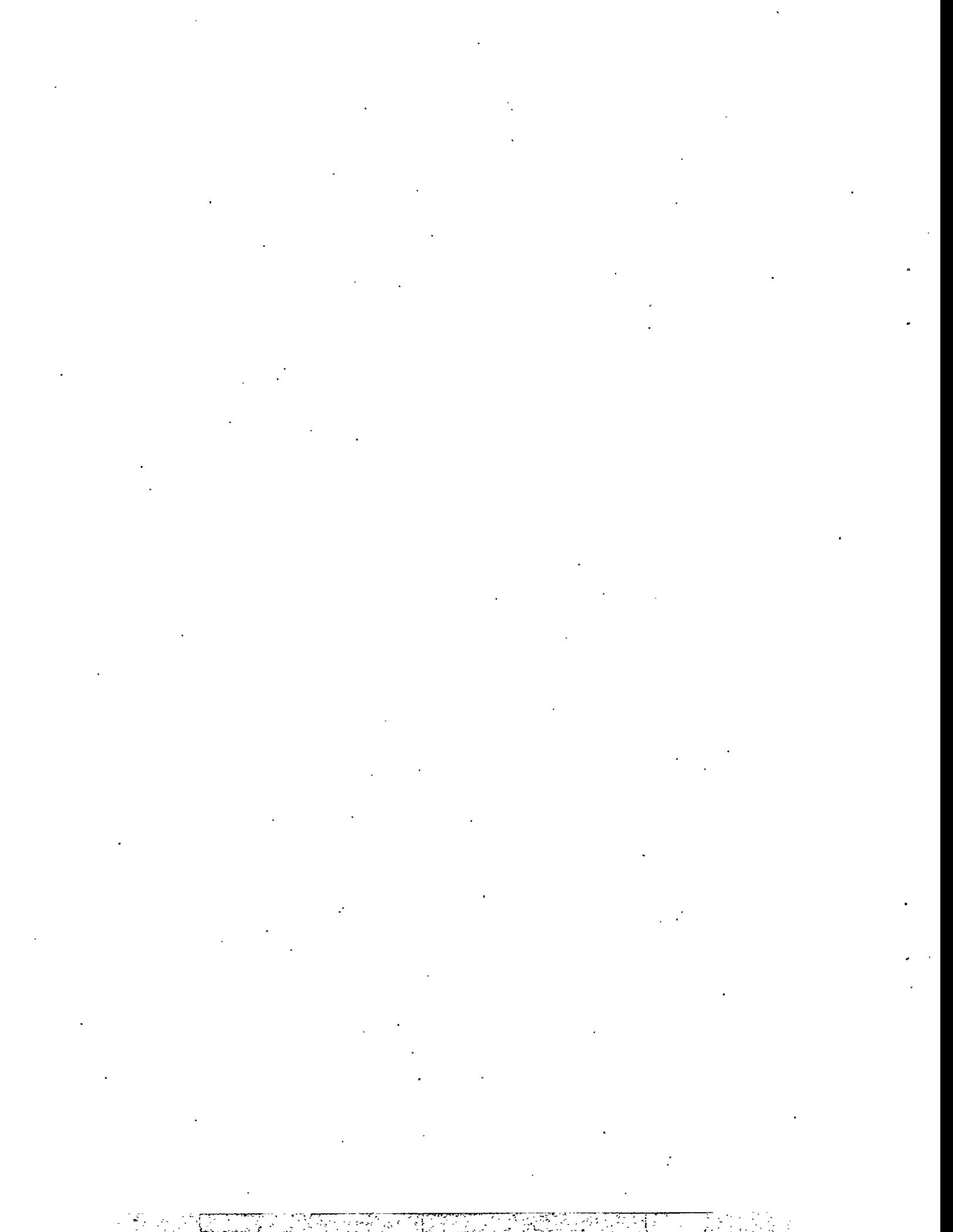
1. Streamlining overall data loading by working with the laboratories to provide electronic data
2. Working with the TWINS staff to automate the loading process
3. Automating the data validation process
4. Providing sample and analysis averages of data by tank
5. Fully implementing the unit conversion capabilities
6. Searching the data with greater flexibility (such as by chemical synonyms, CAS number, or compound class)
7. Continuing to work with the TWINS staff to enhance the interface including improved context sensitive help and sorting capabilities
8. Exploring options for loading toxicology data
9. Loading historical and current data from the standard hydrogen monitoring system.

7.0 Conclusions/Lessons Learned

Progress was made during FY 1995 in all aspects of work supporting the characterization of vapor in the headspaces of waste tanks at Hanford. Thanks to operational improvements in the VSS by the WHC staff responsible for performing vapor jobs and obtaining samples, the repeatability of samples improved during the year. In addition, the type and number of samples provided to WHC for each sample job were altered over the year and evolved into a set of samples that provides a good compromise between minimizing cost and meeting analytical objectives. Analytically, instrumentation was obtained and upgraded to support characterization of inorganic, permanent gas, and organic constituents. The technical procedures used in the PNL vapor analytical laboratory were improved during two periods of upgrades to the quality assurance level of the project; first when procedures were upgraded to PNL Impact Level II and second when a new procedure was developed to support analysis of thermal desorption (triple sorbent trap) samples. Final changes were also made to the procedures in response to comments received during quality assurance assessments after both phases of this work. Also, an effort to provide additional improvement to quality assurance and quality control was initiated late in FY 1995 on receipt of direction from WHC for the project to achieve compliance with HASQAP in early FY 1996.

Associated with the lessons learned and improved sampling and analytical operations were improvements in the understanding of the technical basis for the need to characterize the vapors present in tank headspaces. Support for this work was provided by PNL beginning in mid-year. Although influenced by a complex variety of data quality objectives for a number of different programs, the general consensus of an evaluation was that vapor data obtained by the project provide a technically justified contribution to the overall objective of characterizing the waste contents of tanks. Also resulting from the technical basis work, closer integration with other elements of TWRS has led to other improvements initiated in FY 1995 or planned for FY 1996. These include incorporation of HASQAP using the knowledge base of the PNL Analytical Chemistry Laboratory, the streamlining of data reports and vapor input for Tank Characterization Reports, and full integration of the tank vapor database with the TWINS-based tank characterization database.

Increased knowledge of the vapor constituents present in tanks has led to recommendations by WHC and PNL staff for continued work based on cost-saving sampling and analytical methods and approaches. Key among these is the recommendation to shift from a vehicle-based sampling system (the VSS) to a cart-based system (the ISVS). This approach, if validated early in FY 1996, will save significantly on operational costs associated with fabrication, cleaning, and crane-supported installation of the water-heated vapor probes needed by the VSS. It will also save operational costs associated with maintenance and operation of the sampling system. Analytically, a tentative decision was made to speciate organic compounds in only selected tanks rather than all tanks. Data was also obtained in FY 1995, and additional data will be obtained in early FY 1996, that will allow a comparison of results obtained from the SUMMA™ and the thermal-desorption sampling and analytical methods for providing speciation of the organic constituents in tank headspaces. Important to this comparison will be the ISVS-supported ability to obtain samples more directly from the tank headspaces than was possible using the VSS. Although both methods are employed now, because each has independent value and each lacks full validation, it is possible that one or the other method may ultimately be selected as the primary method of speciating organic compounds. This would allow the other method to be retained but to be limited to specific analyses (permanent gases and total non-methane hydrocarbons in the case of SUMMA™ samples and semivolatile compounds in the case of thermal desorption samples).



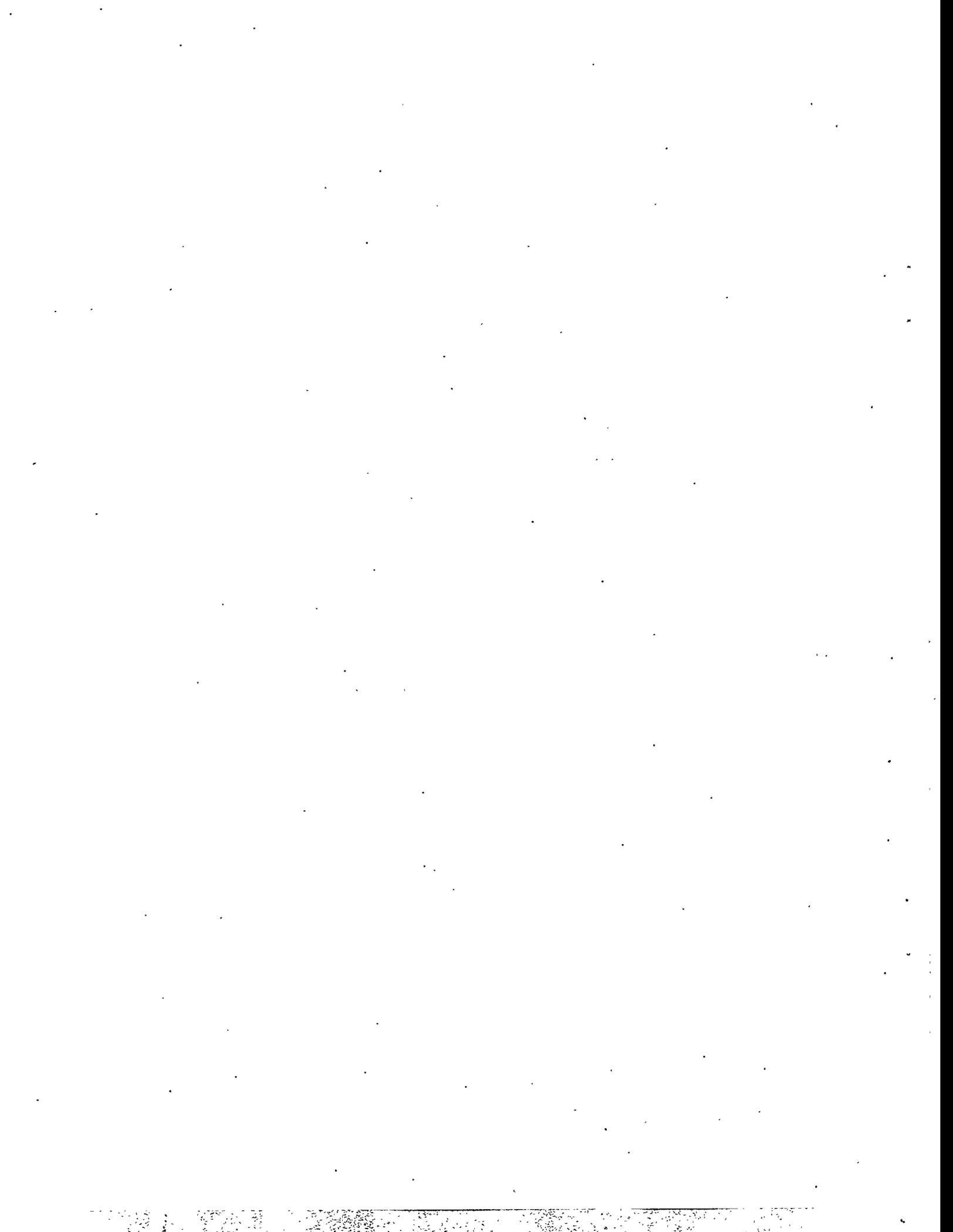
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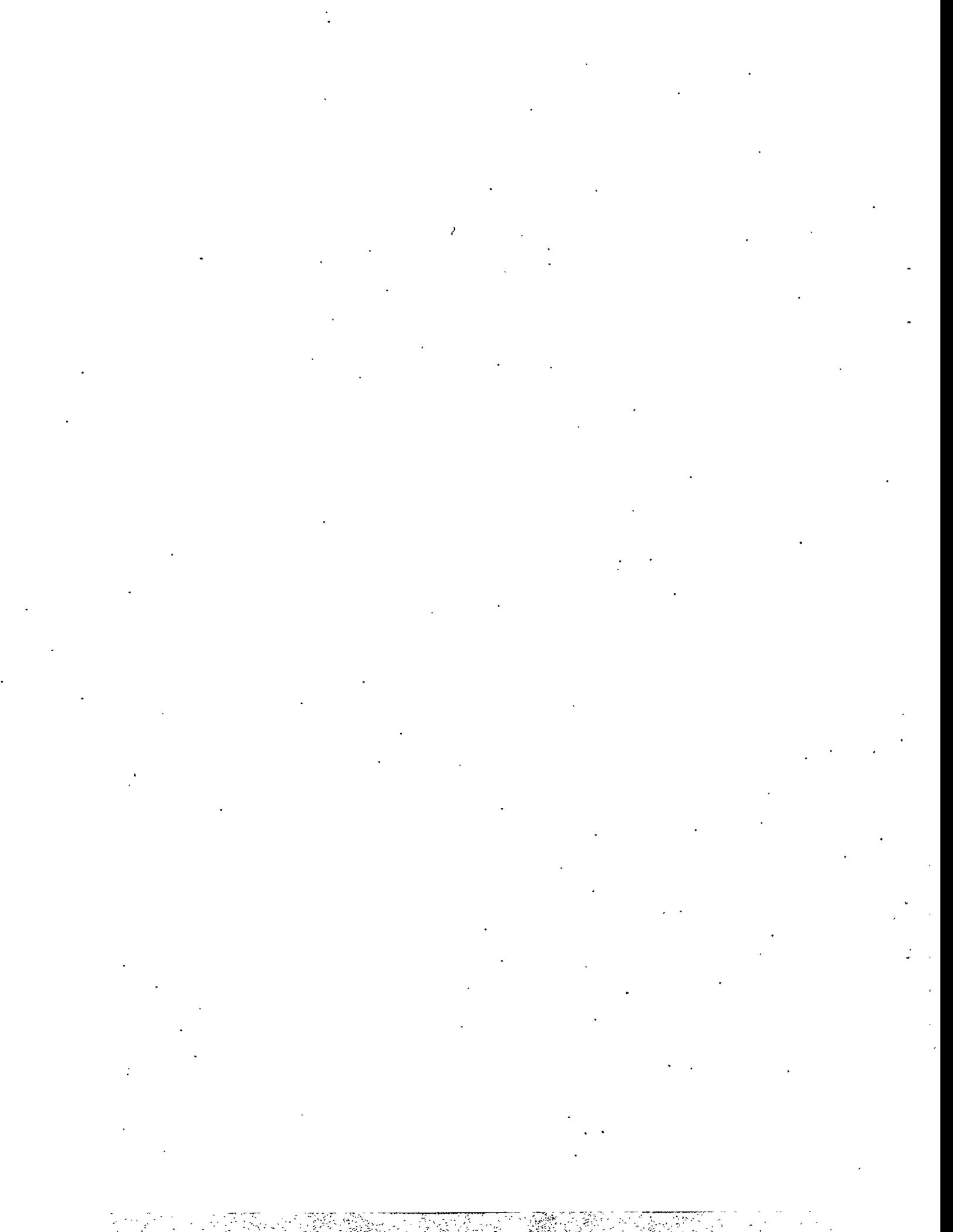
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Appendix A

List of Current Technical Procedures for the PNL Tank Vapor Characterization Project

<u>Procedure</u>	<u>Date</u>	<u>Title</u>
PNL-TVP-01, Rev. 0	August 1994	Determination of TO-14 volatile organic compounds in ambient air using SUMMA™ passivated canister sampling and gas chromatography/mass spectrometry (GC/MS) analysis.
PNL-TVP-02, Rev. 0	August 1994	Cleaning SUMMA™ canisters and the validation of the cleaning process
PNL-TVP-03, Rev. 0	August 1994	Determination of TO-14 volatile organic compounds in Hanford waste tank headspace samples using SUMMA™-passivated canister sampling and gas chromatography/mass spectrometry analysis.
PNL-TVP-05, Rev. 0	December 1994	Analysis method for the determination of permanent gases in Hanford waste tank vapor samples collected in SUMMA™-passivated stainless steel canisters.
PNL-TVP-06, Rev. 0	November 1994	Preparation of TO-14 volatile organic compound gas standards.
PNL-TVP-07, Rev. 1	June 1995	Shipping, receiving, and handling procedure for PNL waste tank samples.
PNL-TVP-08, Rev. 0	June 1995	Determination of TO-12 total nonmethane organic compounds in Hanford waste tank headspace using SUMMA™ passivated canister sampling and flame ionization detection.
PNL-TVP-09, Rev. 1	April 1995	Sorbent trap preparation for sampling and analysis: waste tank inorganic vapor samples.
PNL-TVP-10, Draft	July 1995	Determination of volatile organic compounds in Hanford waste tank headspace samples using triple sorbent trap (TST) sampling and gas chromatography/mass spectrometry (GC/MS) analysis.



Appendix B

Inorganic Task Vapor Sample Hold Time Study

Method validation work performed to test methods used by the inorganic task to date have included samples and controls used in selected vapor sample jobs performed in FY 1994 and a hold-time study performed in FY 1995.

B.1 Inorganic Method Validation in FY 1994 (In-Tank)

In FY 1994, some samples or blanks provided to WHC and used to sample waste tank headspaces were spiked before sampling with known quantities of target analytes. The percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol of NH_3 were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively (Clauss et al. 1994, Ligothke et al. 1994). Results of sorbent traps spiked before sampling with 24 and 48 μmol of NH_3 were within 3% of unspiked samples when corrected for the spike quantities (Ligothke et al. 1994). In that case, approximately 44 μmol of NH_3 were actually collected in samples from the tank. The percentage recoveries of blanks spiked with 0.0064, 0.047, 0.11, and 0.74 μmol of NO_2^- were $153 \pm 14\%$, $103 \pm 4\%$, $106 \pm 8\%$, and $111 \pm 7\%$, respectively (Clauss et al. 1994, Ligothke et al. 1994). The relatively poor result for the 0.0064 μmol spike was likely the result of a very small quantity of analyte spiked on to the sorbent media (equivalent to an air concentration of ~ 0.1 ppmv NO_2). The percentage recovery from blanks spiked with 51 mg of water was $103 \pm 2\%$ (Clauss et al. 1994).

B.2 Inorganic Method Validation in FY 1995 (Hold-Time Study)

The hold-time study performed in FY 1995 was intended to evaluate the effect of variations in the processing and analysis of samples for NH_3 , NO_2 , NO , and H_2O . A series of tests was conducted to determine whether the time interval between sample collection and actual analysis in any way affected analytical results. Variations of the time interval between sample loading on sorbent tube materials and disassembly and exposure to desorbing solution, as well as the time interval between exposure to desorbing solution and actual analysis, were examined. Both ammonia and NO_x sorbent traps were included in this study. The time intervals examined included extreme cases that bracketed realistic time intervals actually encountered in the tank vapor project to date. The hold time study consisted of five separate tests.

Analyte Loading onto Sorbent Traps Known quantities of standard solutions of NaNO_2 , NH_4Cl , or water were injected into the front, or primary, sections of NH_3 , NO_x , and H_2O sorbent traps, respectively. Gas-tight syringes were used to make the injections. The loaded sorbent traps were sealed with plastic end caps provided by the sorbent trap vendor (SKC) and stored in a refrigerator ($< 10^\circ\text{C}$) until weighed (all traps), disassembled, and the sorbent trap materials exposed to desorbing solutions (NH_3 and NO_x traps). Blanks consisted of traps with no analytes added that were handled and stored exactly the same way as spiked tubes. Desorbing solutions were DIW for NH_3 traps and 1.5% triethanolamine in DIW for NO_x sorbent trap materials.

Hold-Time Test Matrix

- 1) Analyte loading quantities (spike levels). In order to mimic typical sample loading for actual tank vapor space samples, the following assumptions were used:
 - a) Total volume of air sampled equaled 3.00 L.

b) Analyte concentration in vapor sample equals the following levels:

Traps loaded with quantities of analytes simulating the levels that would be trapped from concentrations of 25 ppmv (NH₃) and 1 ppmv (NO₂) were used as the "base case", and for extreme cases, 0.1x and 10x the base case for NH₃ and 10 x the base case for NO₂. For the base case, 56 µg NH₃ and 3.2 µg NO₂⁻ were spiked into the front, or primary, sorbent sections of the appropriate sorbent tubes.

2) Hold Times

a) Load spike onto sorbent tubes to disassemble/desorb time interval.

The base-case interval was four weeks, which is typical of experience with actual tank vapor sampling events (Test H101). Extreme case intervals were one week and four months (Test H102).

b) Disassemble and desorb to actual analysis time interval (Contact time).

The base case contact time was 3 days. Extreme case intervals were two weeks and approximately 1 h, which is the shortest practical time needed to carry out the laboratory operations (Test H101). Sorbent tube materials exposed to desorbing solutions were maintained at laboratory ambient temperature.

3) Sorbent trap trains versus individual tubes. Base case hold times and spike levels were used in a test to determine if spiked sorbent tubes in the typical train configuration used for actual sampling of waste tank vapor space would give the same results (analyte recovery) as individually spiked and stored sorbent tubes (Test H103).

4) Replicates. Three or five samples and one blank were included for each hold-time interval and spike level used except the base case test (Test H101), which included five samples and three blanks.

Hold-Time Study Results Results of the percentage recovery of NH₃ and NO₂⁻ from sorbent traps are shown in Tables B.1 through B.4. Results of the percentage recovery of water spikes onto silica gel traps are shown in Table B.5. Test H101 (Table B.1) showed that percentage recoveries of analytes varied between 99 to 107% for samples having variable time of contact of sorbent materials with the desorbing solutions ranging from ~ 1 hour to 2 weeks. No clear trend with increased desorbing solution contact time was observed. Test H102 (Table B.2) showed that percentage recovery of analytes varied between 96 and 107% for samples held ~ 1 week to 4 months after spikes were added (and before sorbent media was contacted with desorbing solutions). Again, no trend with sample hold time was observed. Test H103 (Table B.3) showed that the practice of assembling the sorbent traps into trains did not significantly alter analyte recovery. Test H104 (Table B.4) indicated that the quantity of analyte spiked into the sorbent media (over ranges similar to those expected from actual tank headspace samples) did not significantly alter analyte recovery. Finally, Test H105 (Table B.5) showed that, although uncorrected percentage recovery of water spikes was 109 to 118% for the smaller loading level (~ 16 mg per trap), the blank-corrected results indicated a spike recovery of 99 to 103% for both levels of water spikes and for hold times between 1 week and 4 months. In nearly all cases (20 of 23 data sets), one standard deviation of the three or five samples used to calculate each average percentage recovery was between 0 to 5% of the average; in the other three data sets one standard deviation was between 6 and 8% of the average value.

Hold-Time Study Conclusions There were no apparent trends in the recoveries of either ammonia or nitrite from sorbent traps with respect to the hold time and sample handling parameters investigated. Average percentage recoveries varied from 96 to 111%. There were also no apparent trends in the recovery of water with respect to hold time. Sample handling, storage, and analysis practices were shown to provide nonbiased results relative to the requirement to produce results with accuracy between 70 and 130% and precision of less than $\pm 25\%$ for analytes found in the range of typical, expected, or greater-than-expected concentrations. (It should be noted that the range of analyte loading tested for NH_3 was limited to levels expected for concentrations between 2.5 and 250 ppmv; although greater levels have been found in tank samples [some exceeding 1000 ppmv], analysis of such samples has indicated no breakthrough from the primary to the secondary sorbent layers has ever occurred. Thus, the results of this hold time study are expected to be applicable to concentrations up to and exceeding 1000 ppmv. Should any greater concentration of NH_3 be found that actually causes breakthrough to the secondary layer, additional method validation work would be suggested.)

Table B.1 Summary Results of Hold-Time Study - Base Case Including Extremes in Contact Time (Test H101)

Test:	H101
Spike Levels:	NH ₃ , 56 µg/trap front section (~ 25 ppmv) NO ₂ ⁻ , 3.2 µg/trap front section (~ 1 ppmv)
Hold Times:	Load spike to disassemble and desorb = 4 weeks Desorb to analysis = 1 h, 3 days, 2 weeks (contact time with desorbing solutions)
Samples:	5 samples and 3 blanks analyzed for each analyte and hold time

Contact Time	NH ₃		NO ₂ ⁻	
	% Recovery	± 1 std. dev.	% Recovery	± 1 std. dev.
~ 1 hour	99	2	104	2
3 days	107	2	104	3
2 weeks	104	2	103	3

Table B.2 Summary Results of Hold-Time Study - Extreme Load to Disassemble Time Intervals

Test:	H102
Spike Levels:	NH ₃ , 57 µg/trap front section (~ 25 ppmv) NO ₂ ⁻ , 3.2 µg/trap front section (~ 1 ppmv)
Hold Times:	Load spike to disassemble and desorb = 1 week, 4 weeks (from Test H101), 4 months Desorb to analysis = 3 days (contact time with desorbing solutions)
Samples:	3 samples and 1 blank analyzed for each analyte and hold time

Load Spike to Disassemble Time	NH ₃		NO ₂ ⁻	
	% Recovery	± 1 std. dev.	% Recovery	± 1 std. dev.
~ 1 week	96	1	100	1
4 weeks (H101)	107	2	104	3
4 months	103	5	104	7

Table B.3 Summary Results of Hold-Time Study - Sorbent Trap Trains versus Individual Sorbent Traps

Test:	H103
Spike Levels:	NH ₃ , 56 µg/trap front section (~ 25 ppmv) NO ₂ ⁻ , 3.2 µg/trap front section (~ 1 ppmv)
Hold Times:	Load spike to disassemble and desorb = 4 weeks Desorb to analysis = 3 days (contact time with desorbing solutions)
Samples:	3 samples and 1 blank analyzed for each analyte and hold time

Sorbent Trap Configuration	NH ₃		NO ₂ ⁻	
	% Recovery	± 1 std. dev.	% Recovery	± 1 std. dev.
Individual Trap	111	2	106	5
Sorbent Train	109	1	104	1

Table B.4 Summary Results of Hold-Time Study - Variation of Spike Levels

Test:	H104
Spike Levels:	NH ₃ , 5.6 and 570 µg/trap front section (~ 2.5 and 250 ppmv) NO ₂ ⁻ , 32 µg/trap front section (~ 10 ppmv)
Hold Times:	Load spike to disassemble and desorb = 4 weeks Desorb to analysis = 3 days (contact time with desorbing solutions)
Samples:	3 samples and 1 blank analyzed for each analyte and hold time

Analyte Spike Load	NH ₃		NO ₂ ⁻	
	% Recovery	± 1 std. dev.	% Recovery	± 1 std. dev.
5.6 µg NH ₃	105	8		
56 µg NH ₃ (H101)	107	2		
570 µg NH ₃	104	2		
3.2 µg NO ₂ ⁻ (H101)			104	3
32 µg NO ₂ ⁻			99	6

Table B.5 Summary Results of Hold-Time Study - Gravimetric (Water) Study

Test:	H105
Spike Levels:	H ₂ O, 16 and 60 mg per trap (~ 5 and 20 mg/L)
Hold Times:	Load spike to weigh trap = 1 week, 4 weeks, 4 months
	Desorb to analysis = n/a
Samples:	3 samples and 1 blank analyzed for each load level and hold time

<u>Hold Time</u>	<u>Load</u>	<u>Uncorrected Data</u>		<u>Blank-Corrected Data</u>	
		<u>% Recovery</u>	<u>± 1 std. dev.</u>	<u>% Recovery</u>	<u>± 1 std. dev.</u>
1 week	16 mg	110	2	101	2
1 week	60 mg	105	1	102	1
4 weeks	16 mg	109	1	103	1
4 weeks	61 mg	101	0	100	0
4 months	16 mg	118	2	101	2
4 months	60 mg	104	0	99	0

Appendix C

Waste Tank Vapor Characterization Data Reports

(Page 1 of 2)

TANK	JOB	DATE	VAPOR DATA REPORTS				TCR CHAPTERS	
			DRAFT	CLEARANCE	FINAL	PNL NO.	DRAFT	FINAL
PBI-Related Vapor Jobs:								
B-103	S5003	2/8/95	3/17/95	9/20/95	Oct '95	10704	5/95	Oct '95
BX-104	S4089	12/30/94	4/7/95	8/2/95	Oct '95	10642	5/95	Oct '95
BY-103	S4080	11/1/94	3/10/95	9/20/95	Oct '95	10703	5/95	Oct '95
BY-104	S4019	6/27/94	9/22/94	10/27/94	Nov '94	10208	5/95	Oct '95
BY-105	S4020	7/7/94	11/3/94	12/20/94	May '95	10256	5/95	Oct '95
BY-106	S4021	7/8/94	11/2/94	9/7/95	Oct '95	10248	5/95	Oct '95
BY-107	S4077	10/26/94	1/27/95	2/24/95	Oct '95	10468	5/95	Oct '95
BY-108	S4076	10/27/94	2/10/95	3/28/95	Oct '95	10495	5/95	Oct '95
BY-110	S4082	11/11/94	2/17/95	3/29/95	Jun '95	10505	5/95	Oct '95
BY-111	S4083	11/16/94	3/3/95	6/8/95	Jun '95	10599	5/95	Oct '95
BY-112	S4084	11/18/94	3/17/95	6/8/95	Jun '95	10598	5/95	Oct '95
C-101	S4056	9/1/94	2/3/95	3/16/95	Nov '95	10491	5/95	Oct '95
C-102	S4057	8/23/94	5/3/95	7/28/95	Oct '95	10646	5/95	Oct '95
C-104	n/a	3/3/94	1/19/95	9/15/95	Oct '95	10499	5/95	Oct '95
C-105	n/a	2/16/94	1/19/95	10/31/95	Jun '95	10466	5/95	Sep '95
C-106	n/a	2/15/94	1/20/95	1/28/95	Jun '95	10498	5/95	Oct '95
C-107	S4058	9/29/94	1/27/95	10/31/95	Nov '95	10736	5/95	Oct '95
C-108	S4052	8/5/94	11/30/94	9/13/95	Oct '95	10351	5/95	Oct '95
C-109	S4053	8/10/94	12/21/94	2/8/95	Jun '95	10418	5/95	Oct '95
C-110	S4059	8/18/94	4/28/95	7/28/95	Oct '95	10645	5/95	Oct '95
C-111	S4060	9/13/94	12/16/94	2/8/95	May '95	10390	5/95	Oct '95
C-112	S4054	8/11/94	1/27/95	8/2/95	Oct '95	10643	5/95	Oct '95
S-102	S5015	3/14/95	4/21/95	8/2/95	Oct '95	10587	5/95	Oct '95
SX-106	S5018	3/24/95	4/26/95	10/31/95	Nov '95	10584	5/95	Oct '95
T-107	S5001	1/18/95	3/24/95	6/8/95	Jun '95	10595	5/95	Oct '95
TX-105	S4087	12/20/94	3/10/95	6/8/95	Jun '95	10594	5/95	Oct '95
TX-118	S4088	12/16/94	3/31/95	8/2/95	Oct '95	10625	5/95	Oct '95
TY-101	S5019	4/6/95	5/8/95	10/31/95	Nov '95	10706	5/95	Oct '95
TY-103	S5020	4/11/95	5/4/95	8/2/95	Oct '95	10644	5/95	Oct '95
TY-104	S5021	4/27/95	5/12/95	7/8/95	Oct '95	10647	5/95	Oct '95
U-106	S5012	3/7/95	3/31/95	6/8/95	Jul '95	10593	5/95	Oct '95
U-107	S5008	2/17/95	4/14/95	9/20/95	Oct '95	10729	5/95	Oct '95
U-111	S5009	2/28/95	4/19/95	6/1/95	Jul '95	10588	5/95	Oct '95
Safety-Related Vapor Jobs:								
A-101	S5026	6/8/95	9/27/95	11/15/95	Nov '95	10808	9/95	Oct '95
AX-102	S5035	6/27/95	9/27/95	11/15/95	Nov '95	10809	9/95	Oct '95
S-111	S5016	3/21/95	6/20/95	9/20/95	Oct '95	10733	9/95	Oct '95
SX-103	S5017	3/23/95	6/23/95	10/31/95	Nov '95	10814	9/95	Oct '95
T-111	S5002	1/20/95	5/25/95	8/15/95	Oct '95	10648	9/95	Oct '95
U-103	S5007	2/15/95	6/2/95	10/31/95	Nov '95	10813	9/95	Oct '95
U-105	S5011	2/24/95	6/9/95	9/20/95	Oct '95	10702	9/95	Oct '95
U-203	S5036	8/9/95	9/27/95	11/15/95	Nov '95	10812	9/95	Oct '95
U-204	S5037	8/8/95	9/27/95	11/15/95	Nov '95	10811	9/95	Oct '95

Waste Tank Vapor Characterization Data Reports

(Page 2 of 2)

TANK	JOB	DATE	VAPOR DATA REPORTS				TCR CHAPTERS	
			DRAFT	CLEARANCE	FINAL	PNL NO.	DRAFT	FINAL
Sample Jobs in C-103:								
C-103	n/a	11/29/93			Sep '94	10079	n/a	n/a
C-103	n/a	12/2/93			Mar '94	9368	n/a	n/a
C-103	n/a	5/12/94			Jun '95	10388	n/a	n/a
C-103	n/a	5/12-25/94			Oct '94	10172	n/a	n/a
C-103	n/a	5/18,24/94			Sep '94	10081	n/a	n/a
Other Vapor Jobs:								
AX-101	S5028	6/15/95	8/2/95					
AX-103	S5029	6/21/95	8/8/95					
S-112	S5044	7/11/95	9/27/95			10807		
SX-101	S5045	7/21/95	10/19/95					
SX-102	S5046	7/19/95	10/19/95					
SX-104	S5049	7/25/95						
SX-105	S5047	7/26/95						
SX-109	S5048	8/1/95						
U-108	S5054	8/29/95						
U-109	S5055	8/10/95						
T-110	S5056	8/31/95						
In-Situ Vapor Jobs (ISS):								
BY-103	S4026	5/5/94	11/14/94	12/20/94	Jun '95	10280	n/a	n/a
BY-104	S4162	4/22/94	11/18/94	9/13/95	Oct '95	10361	n/a	n/a
BY-105	S4027	5/9/94	11/3/94	12/20/94	May '95	10282	n/a	n/a
BY-106	S4024	5/4/94	11/28/94	12/20/94	Apr '95	10284	n/a	n/a
BY-107	S4014	3/25/94	11/3/94	12/20/94	Jun '95	10257	n/a	n/a
BY-108	S4011	3/24/94	10/25/94	12/20/94	Jun '95	10288	n/a	n/a
BY-109	S4071	9/22/94	12/16/94	2/8/95	Jun '95	10389	n/a	n/a
BY-111	S4028	5/11/94	12/9/94			10368	n/a	n/a
C-101	S4039	7/7/94					n/a	n/a
C-107	S4041	6/16/94	12/21/94	2/8/95	Jun '95	10420	n/a	n/a
C-108	S4045	7/8/94				10351	n/a	n/a
C-109	S4031	6/23/94	12/9/94	9/13/95	Oct '95	10366	n/a	n/a
C-111	S4030	6/20/94	12/9/94	9/13/95	Oct '95	10367	n/a	n/a
C-112	S4032	6/24/94				10810	n/a	n/a
TX-118	S4066	9/7/94			Oct '95	10732	n/a	n/a
TY-101	S4061	8/5/94			Jul '95	10473	n/a	n/a
TY-103	S4062	8/5/94	3/1/95	6/8/95	Jun '95	10597	n/a	n/a
TY-104	S4063	8/5/94	2/24/95	9/20/95	Oct '95	10737	n/a	n/a
U-106	S4067	8/25/94			Oct '95	10730	n/a	n/a

Appendix D

Tank Vapor Database Information

Information supporting the progress made in FY 1995 on the tank vapor database includes a list of tanks for which data was loaded into the database, identifiers assigned to chemicals, a data model, and the database data dictionary.

D.1 Data Loaded into the Tank Vapor Database in FY 1995

Data on the vapor samples collected and analyzed from the following waste tanks at the Hanford Site are loaded into the Tank Vapor Database for the following tanks using information from VSS sampling jobs (e.g., Tank 241-B-103 is referred to as B-103):

B-103, BX-104, BY-104, BY-105, BY-106, BY-103, BY-108, BY-110, BY-111, BY-112, C-102, C-103, C-104, C-105, C-106, C-107, C-109, C-110, C-111, C-112, S-102, SX-106, T-107, TX-105, TX-118, TY-101, TY-103, TY-104, U-103, U-105, U-106, U-107, and U-111.

D.2 Unique Identifiers Assigned to Chemicals in the Tank Vapor Database

The process of assigning unique identifiers, as described in this appendix, is used in the Tank Vapor Database to provide chemical identifiers when Chemical Abstract Services (CAS) numbers are not available. The unique identifiers are assigned to mixtures of compounds or to single compounds whose identities are not well defined. The process, while nontraditional, provides the current and future users and database developers with a logical, rather than an arbitrary, system.

For a single compound that is not well defined or is unknown, the first letter is a U. The next two characters define the primary compound type (see Table B.1). Then, the next three characters give the number of carbon atoms for aliphatic compounds, if known (otherwise, zeros are entered). Then, a hyphen is entered. The last two numbers are a counter system, starting with 01 and incrementing to prevent duplicate numbers from being entered.

For example, the unique identifier UKE011-03 represents an unknown ketone that is aliphatic with 11 carbons. This is the third such unknown 11-carbon ketone to be assigned a unique identifier.

For a mixture, the first character is M. The next four characters define the two primary compound types (see Table D.1). However, either or both sets of two characters may be preceded by a U if either or both compounds, respectively, are not well defined. To prevent redundancies the order for the four to six characters (i.e., the U before the second set of characters does count in the ordering) is alphabetical. If the letter U is not needed in either or both cases, one or two zeros are added after the five or four characters, respectively, defining the compound types. Then, a hyphen is entered. The last two numbers are a counter system, starting with 01 and incrementing to prevent duplicate numbers from being entered. In the case of a mixture of unknowns with no information, MU00000-00 will be used.

D.2.1 Examples of unique identifiers In the case of a mixture that consists of one compound "and others" if the compound has a CAS number, it is used with an M added to the end. If the compound does not have a CAS number (e.g., because it is not well defined) the unique identifier is assigned in the same manner as for a single compound, and an M is added at the end.

Examples of unique identifiers include the following:

MAKOH00-01	is a mixture with a known alkane (e.g., 2-methylheptane) and a known alcohol (e.g., 2-butanol).
MAKUOH0-01	is a mixture with an imprecisely defined alkane (e.g., C ₈ -alkane) and a known alcohol.
MAKUOH0-01	is a mixture with a known alkane and an imprecisely defined alcohol (e.g., butanol).
MUAKUOH-01	is a mixture in which both alkane and alcohol are not well defined.

Table D.1 Tank Vapor Database Unique Identifiers Compound Types

Compound Designation	Type
AA	Acid anhydrides (aliphatic or aromatic)
AD	Aldehydes (aliphatic or aromatic)
AE	Alkenes
AH	Alkyl halides
AK	Alkanes
AM	Amines (aliphatic or aromatic)
AR	Aromatics, hydroaromatics, arenes
AY	Alkynes
CA	Carboxylic acids (aliphatic or aromatic)
CY	Cycloalkanes, cycloalkenes, cycloalkynes
ES	Esters (aliphatic or aromatic), includes cyclic esters such as lactones
ET	Ethers (aliphatic or aromatic)
HC	Heterocyclics
HY	Hydrazine
IN	Inorganic
KE	Ketones (aliphatic or aromatic)
MD	Amides (aliphatic or aromatic)
NA	Nitric acid derivatives
NI	Nitriles (aliphatic or aromatic)
NT	Nitro compounds (aliphatic or aromatic)
OH	Alcohols, glycols
PH	Phenols
PT	Phosphorus containing, including phosphates, phosphonates
RH	Aryl halides
SA	Sulfonamides
SI	Silicon containing (including trimethylsilyl derivatives)
TH	Thiol esters

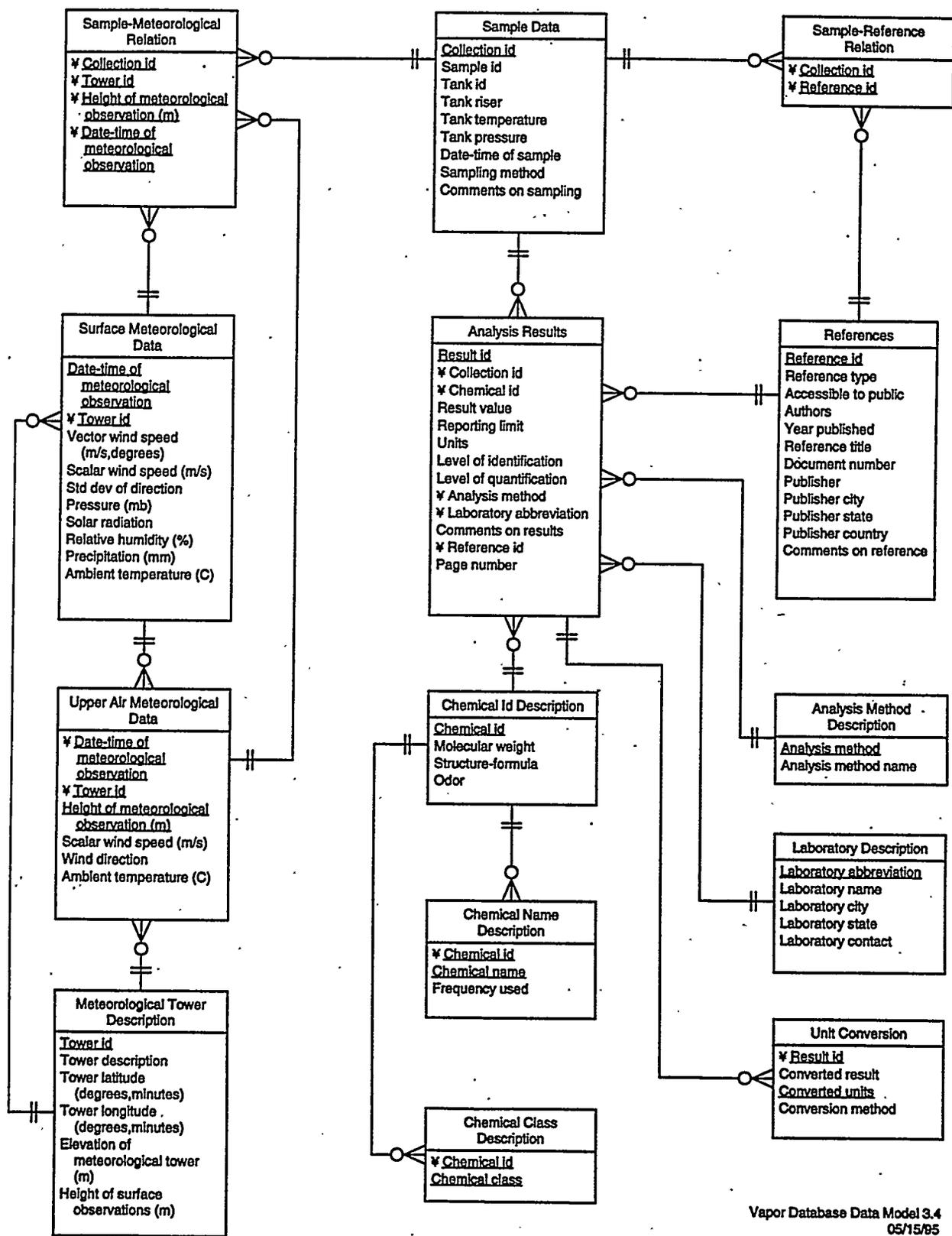
D.3 Tank Vapor Database Data Model

See page D.3.

D.4 Tank Vapor Database Data Dictionary

See pages D.4 - D.16.

Figure D.1 Tank Vapor Database Data Model



Vapor Database Data Model 3.4
05/15/95

Tank Vapor Chemistry Data Dictionary

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Accessible to public	If a Pacific Northwest Laboratory reference is not available to the public, a N appears in this field. If a Pacific Northwest Laboratory reference is available to the public, a Y appears. This field does not apply to other references	Y N	References	No	Yes	char 1
Ambient temperature	Temperature of the air around a meteorological tower (units are °C). The ambient temperature is reported as a 15-minute average	10°C	Surface Meteorological Data	No	Yes	float
Analysis method	Primary instrumentation used to analyze a sample (a sample is defined as a discrete quantity of material collected for analysis). If the sample does not involve a specific instrument (for example, gravimetric analysis), then a general description is reported	GC/FID	Upper Air Meteorological Data Analysis Method Description	No Yes	Yes No	float varchar 50
Analysis method name	Description of the method used to analyze the sample	Gas chromatograph with flame ionization detector	Analysis Results Analysis Method Description	No No	Yes No	varchar 50 varchar 255
Authors	People listed (by first and middle initial and last name) as writers. If authors are not listed, then the name of the company that produced the reference is reported. If a company is not listed, then the word "Anonymous" is reported	K. L. Manke, M. B. Blim, P. R. Seesing EPA Anonymous	References	No	No	varchar 255

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Chemical class	Functional group category to which the constituent belongs	Ketone Alkane	Chemical Class Description	Yes	No	varchar 50
Chemical id	Chemical Abstract Services (CAS) number or appropriate code that uniquely identifies a chemical (a chemical is defined as an element or a compound, which includes radionuclides)	67-66-3 109-79-5	Analysis Results	No	No	char 15
			Chemical Class Description	Yes	No	char 15
			Chemical Id Description	Yes	No	char 15
			Chemical Name Description	Yes	No	char 15
			Physical and Chemical Properties	Yes	No	char 15
			Regulatory Limits	Yes	No	char 15
			Route of Health Hazard	Yes	No	char 15
			Symptoms	Yes	No	char 15
			Tank Averages	Yes	No	char 15
			Vapor Pressure Property	Yes	No	char 15
Chemical name	Name of a chemical (a chemical is defined as an element or a compound, which includes radionuclides)	Hexane Hexyl hydride	Chemical Name Description	Yes	No	varchar 240

Entity Name Description Examples Table Name Key Field? Can be Null? Type/Length

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Collection Id	System-generated code used to make each sample record unique. This code is internal to the database and should not be used for tracking purposes	System generated	Analysis Results	No	No	char 12
Comments on reference	Any additional information that might help the user find the reference	This journal title changed to Kline's Vapor Studies in January 1994.	References	No	Yes	varchar 255
Comments on results	Any concerns or unusual information about the results	Corrected for possible contamination attributed to painting in adjacent laboratory during trap analysis.	Analysis Results	No	Yes	varchar 255
Comments on sampling	Any concerns or unusual information about collecting the sample (a sample is defined as a discrete quantity of material collected for analysis)	Valve connection was contaminated. The sampling amount is in question.	Sample Data	No	Yes	varchar 255
Conversion method	Mathematical formula showing what conversion was performed (any assumptions required to make the calculation are also included)	mg/m3 = (ppmv x molecular weight)/26.21 This assumes average tank conditions with temperature equal to 38°C and a pressure of 740 torr.	Unit Conversion	No	Yes	varchar 255

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Converted result	Converting a reported analytical value with one type of units to another type of units makes the data easier to compare. This field contains the result value that was calculated when the units were converted. For example, if the value was reported as 0°C and the converted units were °F, then the converted result would be 32.	32	Unit Conversion	No	No	float
Converted units	Converting a reported analytical value with one type of units to another type of units makes the data easier to compare. This field contains the units to which the reported value was converted	ppm mg/L	Unit Conversion	Yes	No	char 10
Date-time of meteorological observation	Date and time the meteorological data were reported at the meteorological tower	11-11-1993 12:56	Sample-Meteorological Relation	Yes	No	datetime
Date-time of sample	Date and time the sample was taken (a sample is defined as a discrete quantity of material collected for analysis)	09-09-1993 11:44	Surface Meteorological Data	Yes	No	datetime
Document number	Code assigned by government agencies or government contractors to documents and correspondence they publish; the code is used for tracking purposes. This code includes revision numbers. This code does not include the UC category, which is used by the Office of Scientific and Technical Information	WHC-EP-0474 Rev 1 RL930008765	Upper Air Meteorological Data	Yes	No	datetime
Elevation of meteorological tower	Height above sea level of the base of a meteorological tower (units are meters)	233 m	Sample Data	No	No	datetime
			References	No	Yes	varchar 30
			Meteorological Tower Description	No	Yes	int

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Frequency used	The standard name is the name assigned to the Chemical Abstract Services number. A synonym is any other name associated with the chemical.	Standard Synonym	Chemical Name Description	No	No	char 15
Height of meteorological observation	Vertical distance from the ground to where the surface meteorological measurement was taken (units are meters)	60 m	Sample-Meteorological Relation	Yes	No	int
Height of surface observations	Vertical distance from the base of a meteorological tower to the instruments measuring surface meteorological parameters were located (units are meters)	2 m	Upper Air Meteorological Data Meteorological Tower Description	Yes No	No Yes	int int
Laboratory abbreviation	Acronym of laboratory performing analyses	PNL OGI	Analysis Results	No	No	char 6
Laboratory city	Name of city where the laboratory is located	Richland	Laboratory Description	Yes	No	char 6
Laboratory contact	Telephone number including area code of the main switchboard of the laboratory (using this number is the first step in contacting the laboratory; the switchboard operator should be able to provide other numbers and information)	509-376-7411 1-800-436-2437	Laboratory Description	No	Yes	varchar 30
Laboratory name	Name of laboratory performing analyses	Pacific Northwest Laboratory Oak Ridge National Laboratory	Laboratory Description	No	No	varchar 255

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Laboratory state	Two-letter abbreviation of the state where the laboratory is located	WA	Laboratory Description	No	Yes	char 2
Level of Identification	A constituent is positively identified when specific analytical parameters (for example, retention time, mass spectra) match an authentic standard that was analyzed on the same instrument. A constituent is tentatively identified when there is reasonable evidence to assign a chemical identity, but an authentic standard was not analyzed on the same instrument	Positive Tentative	Analysis Results	No	Yes	char 15
Level of quantification	The concentration is quantified if an instrumental response has been established at several known concentrations of the constituent using an authentic standard (that is, the instrument has been calibrated) and the instrumental response to the constituent is between the lowest and highest known responses (that is, within the calibration range). The concentration is estimated if an instrumental response has not been established for that constituent, yet the analyst reported a concentration for a constituent	Estimated Quantified	Analysis Results	No	Yes	char 15
Molecular weight	Sum of the naturally occurring isotopic atomic weights of all the atoms in a molecule (units are gram/mole)	27.0	Chemical Id Description	No	Yes	float
Odor	Description of the smell associated with a chemical	Pungent Unpleasant	Chemical Id Description	No	Yes	varchar 255
Page number	Page number or range of pages where the information was cited	877 1234-1255	Analysis Results	No	Yes	char 15
			Physical and Chemical Properties	No	Yes	char 15

Entity Name Description Examples Table Name Key Field? Can be Null? Type/Length

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Parameter abbreviation	Acronym of regulatory limit parameter	REL STEL PEL	Regulator Parameter	Yes	No	char 15
Parameter description	Name of regulatory limit parameter	Short-term limit Permissible exposure limit	Regulatory Limits	Yes	No	char 15
Parameter value	Value given for the regulatory parameter	1.0	Regulatory Limits	No	No	float 255
Parameter value units	Units for the value of the regulatory parameter	ppm	Regulatory Limits	No	No	char 10
Precipitation	Amount of precipitation that has fallen in the past hour (units are millimeters)	2 mm	Surface Meteorological Data	No	Yes	float
Pressure	Atmospheric pressure measured at a meteorological tower (units are millibars). The pressure is reported as a 15-minute average	1014 mb	Surface Meteorological Data	No	Yes	float
Property type	A physical or chemical property of a chemical (a chemical is defined as an element or a compound, which includes radionuclides)	Melting point Odor threshold Lower flammability limit	Physical and Chemical Properties	Yes	No	varchar 30
Property units	Units used to report a physical or chemical property	°C ppm	Physical and Chemical Properties	No	No	char 10
Property value	Numeric value of a physical or chemical property of a chemical	2.0	Physical and Chemical Properties	No	No	float
Publisher	Name of company that printed the reference	Pacific Northwest Laboratory Seesing & Grove, Inc.	References	No	Yes	varchar 255

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Publisher city	City where the publisher is located. The actual city should be reported; however, if this is not supplied, the city where the publisher's headquarters are located should be reported	Richland Washington, D.C.	References	No	Yes	varchar 30
Publisher country	Name of the country where the document was printed	Switzerland	References	No	Yes	varchar 30
Publisher state	Two-letter abbreviation of state where the publisher is located. The actual state should be reported; however, if this is not supplied, the state where the publisher's headquarters are located should be reported	WA	References	No	Yes	char 2
Reference id	System-generated code used to make each reference record unique. This code is internal to the database and should not be used for tracking documents	System generated	Analysis Results	Yes	No	char 12
			Physical and Chemical Properties	No	No	char 12
			References	Yes	No	char 12
			Sample-Reference Relation	Yes	No	char 12
Reference title	Title of the reference as it appears on the title page. Subtitles are entered after a colon. If one volume of a set is referenced, then the volume title and volume number should be reported as part of the title	Vapor Studies: Guidelines for a Changing Environment Vol. 5 Risk Communication	References	No	No	varchar 255
Reference type	Library classification of the reference. This is included to make finding the reference easier	Correspondence Report Journal	References	No	No	char 20

Entity Name Description Examples Table Name Key Field? Can be Null? Type/Length

Regulator abbreviation	Acronym of the organization that established the regulatory limit. This may include consensus exposure standard (CES) or other nonregulator abbreviations	OSHA EPA CES	Regulator Description	Yes	No	char	15
Regulator name	Name of organization that established the regulatory limit	National Institute of Occupational Safety and Health	Regulator Description	No	No	varchar	255
Relative humidity	Amount of water vapor in the air (units are %). The relative humidity is reported as a 15-minute average	30%	Surface Meteorological Data	No	Yes	float	
Reporting limit	When the concentration of a constituent cannot be measured below an instrument detection limit or below a contract required quantitation limit, the concentration is shown as less than a lower limit. This is a text field and cannot be included in numerical calculations. For more information on reporting limits, see the corresponding references	< .04	Analysis Results	No	Yes	char	20
Result id	System-generated code to make each results record unique. This code is internal to the database and should not be used for tracking results	System generated	Analysis Results	Yes	No	char	12
Result value	The estimated or quantified concentration of a chemical	13.55	Sample Data	Yes	No	char	12
			Unit Conversion	Yes	Yes	char	12
			Analysis Results	No	Yes	float	

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Route abbreviation	Abbreviation of toxicologically important routes of entry into the human body. NIOSH only lists four possible routes	Inh Abs	Route of Health Hazard	Yes	No	char 4
Route of health hazard description	Definition of the route of health hazard abbreviations	Inhalation Ingestion	Route of Health Hazard Description	Yes	No	char 4
Sample id	Code assigned to a sample by the collecting organization (a sample is defined as a discrete quantity of material collected for analysis)	94081143205	Sample Data	No	Yes	varchar 45
Sampling method	Description of the type of container or general method used to collect a sample (a sample is defined as a discrete quantity of material collected for analysis)	SUMMA canister OVS tube	Sample Data	No	No	char 20
Scalar wind speed	Magnitude of average velocity vector (units are meter/second). The scalar wind speed is reported as a 15-minute average	2.3 m/s	Surface Meteorological Data	No	Yes	float
Solar radiation	Amount of direct short-wave electromagnetic radiation received at a meteorological tower (units are W/m ²). The solar radiation is reported as a 1-hour average	75 W/m ²	Surface Meteorological Data	No	Yes	float
Std dev of direction	Amount of variation in wind direction (units are degrees)	2°	Surface Meteorological Data	No	Yes	float

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Structure-formula	Structural notation for a chemical	CH3CHO	Chemical Id Description	No	Yes	varchar 255
Symptom abbreviation	Abbreviation of a potential symptom of exposure to a chemical	Irrit eyes Weak Ftg	Symptom Description	Yes	No	char 15
Symptom description	Description of acute (short term) symptoms caused by exposure to a chemical (chronic symptoms are not included in the database)	Giddiness Malaise	Symptoms	Yes	No	char 15
Tank id	Code that identifies each tank in a tank farm system	241-C-103 241-SY-101	Sample Data	No	Yes	char 15
Tank pressure	Barometric pressure measured inside of the tank when the sample was taken (units are torr)	0.8 atm	Sample Data	No	Yes	float
Tank riser	Riser number on the waste tank from which the sample was taken (a sample is defined as a discrete quantity of material collected for analysis)	7	Sample Data	No	Yes	char 5
Tank temperature	Temperature inside the waste tank when the sample was taken (units are °C) (a sample is defined as a discrete quantity of material collected for analysis)	100°C	Sample Data	No	Yes	float
Tower description	Location and/or type of meteorological tower	200 West Tower Portable C-Farm Tower	Meteorological Tower Description	No	No	varchar 30
Tower id	Code that identifies a meteorological tower where the data were collected	C01 HO9	Meteorological Tower Description	Yes	No	char 4

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Tower Id	Code that identifies a meteorological tower where the data were collected	C01 HO9	Sample-Meteorological Relation	Yes	No	char 4
			Surface Meteorological Data	Yes	No	char 4
			Upper Air Meteorological Data	Yes	No	char 4
Tower latitude	Latitude of meteorological tower (units are degrees and minutes)	46°34'	Meteorological Tower Description	No	Yes	int
Tower longitude	Longitude of meteorological tower (units are degrees and minutes)	119°36'	Meteorological Tower Description	No	Yes	int
Units	Units used to measure the result value or the reporting limit	mg/L L %	Analysis Results	No	No	char 10
Vapor pressure	Partial pressure of the vapor in equilibrium over the solid or the liquid phase	630	Vapor Pressure Property	No	No	float
Vapor pressure temperature	Temperature at which the vapor pressure was determined (units are °C)	25°C	Vapor Pressure Property	Yes	No	float
Vapor pressure units	Units used to specify the vapor pressure for a chemical	mm Hg	Vapor Pressure Property	No	No	char 10
Vector wind speed	Vector speed of the wind, measuring both magnitude and direction (units are meters/second and degrees). The vector wind speed is reported as a 15-minute average	5 m/s 240°	Surface Meteorological Data	No	Yes	float
Wind direction	Direction of wind at a specific level on a meteorological tower (units are degrees)	170°	Upper Air Meteorological Data	No	Yes	int

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Year published	Year the reference was published according to the title page	1994	References	No	No	char 4

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