

Pacific Northwest National Laboratory

Operated by Battelle for the
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TANK VAPOR CHARACTERIZATION PROJECT

Tank Vapor Characterization Project: Annual Status Report for FY 1996

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Prepared for Westinghouse Hanford Company
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with the U.S. Department of Energy
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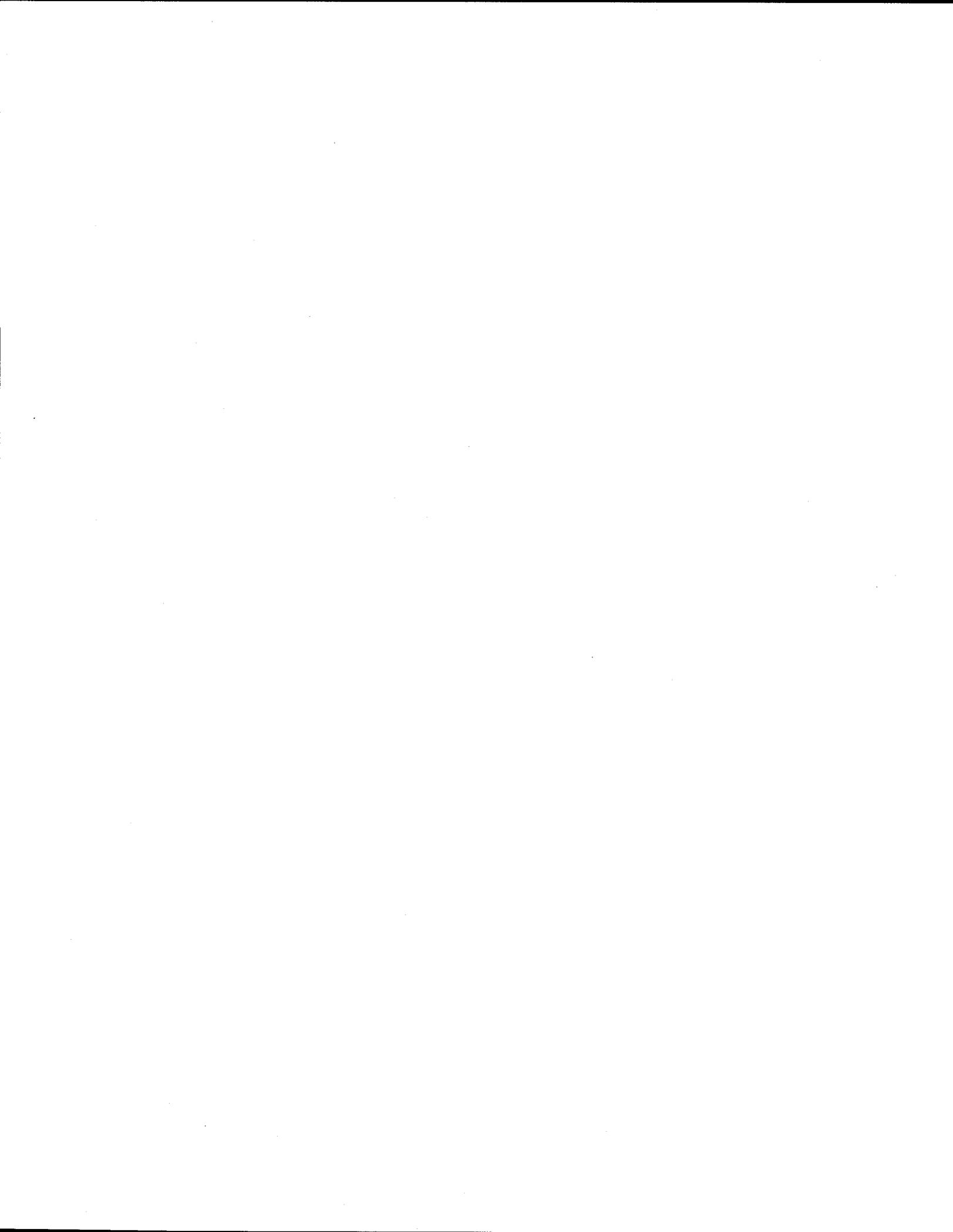
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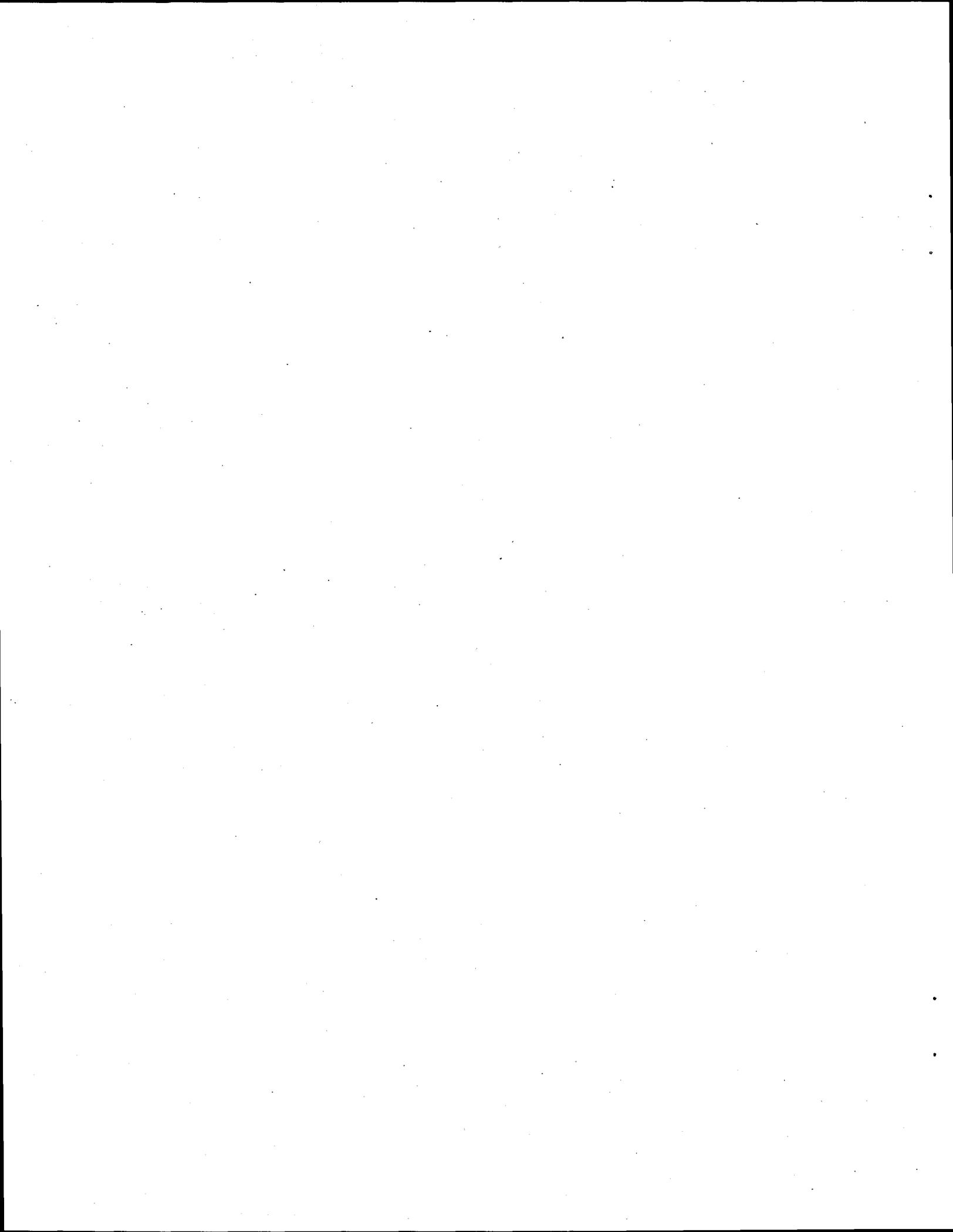
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Summary

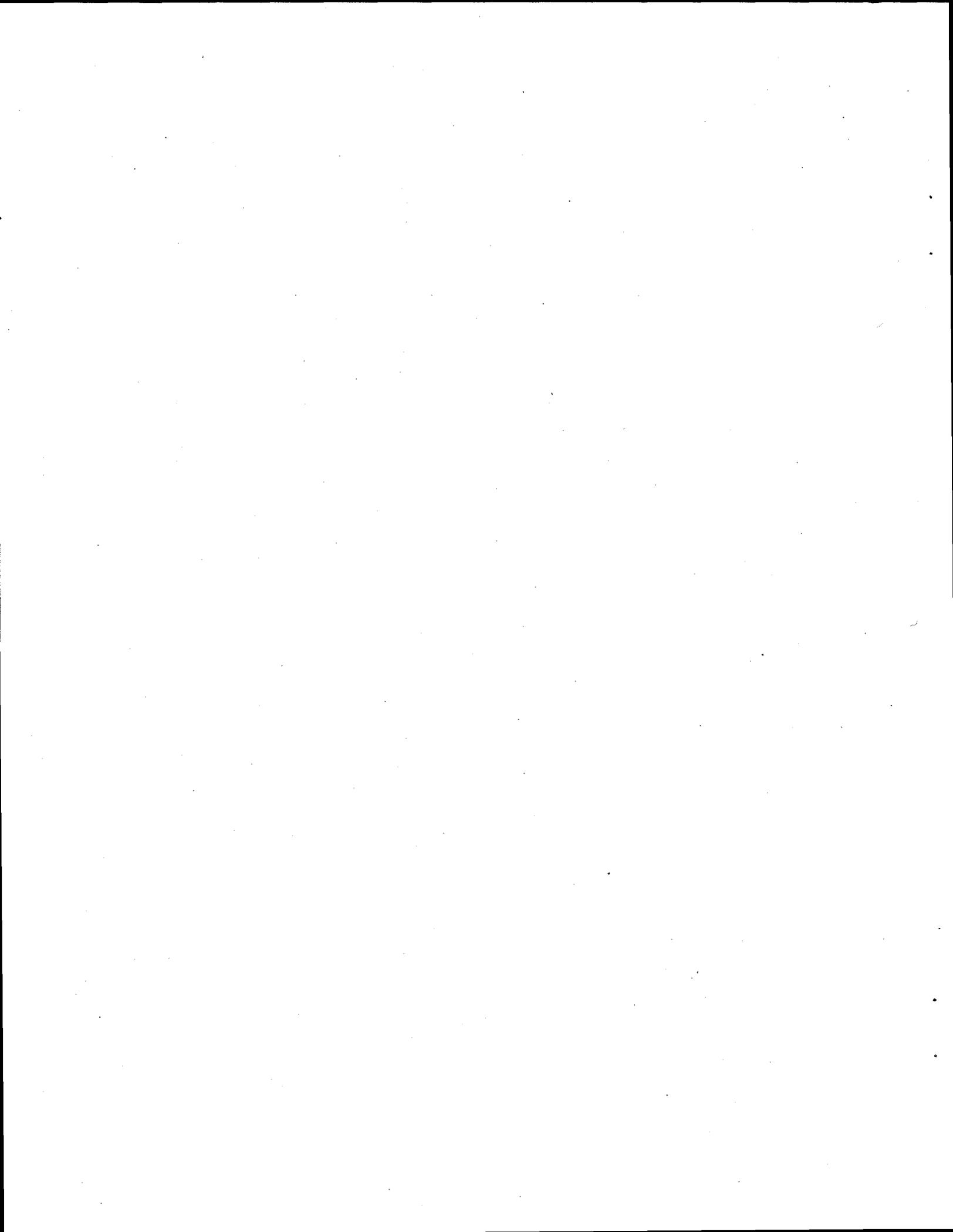
In Fiscal Year (FY) 1996, staff at the Vapor Analytical Laboratory (VAL) at Pacific Northwest National Laboratory (PNNL) performed work in support of characterizing the vapor composition of the headspaces of radioactive waste tanks at the Hanford Site in Southeastern Washington. The work was supported 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 headspaces samples, preparation of data reports, and operation of the tank vapor database. Work performed in FY 1996 was a continuation of work initiated with the first vapor sample job, which was performed in December, 1993.

Progress made in FY 1996 included completion and issuance of 50 analytical data reports. This exceeded the MYPP requirement for 48 data reports. All 50 data reports will be submitted for the November 29, 1996 milestone T24-97-138.

Several key sampling and analysis activities were undertaken in FY 1996. A sampling system comparison study was initiated and completed during the fiscal year. The comparison study involved the vapor sampling system (VSS), a truck-based system, and the in situ vapor sampling system (ISVS), a cart-based system. The study included the sampling of three different tanks (i.e., S-102, C-107, and BY-108) with a wide variety of sampling conditions. Samples collected during the study were characterized for inorganic, permanent gases, total non-methane organic compounds (T0-12), and organic speciation by SUMMA™ and TST methods. The study showed comparable sampling results between the systems resulting in the program switching from the VSS to the less expensive ISVS methodology in late May 1996.

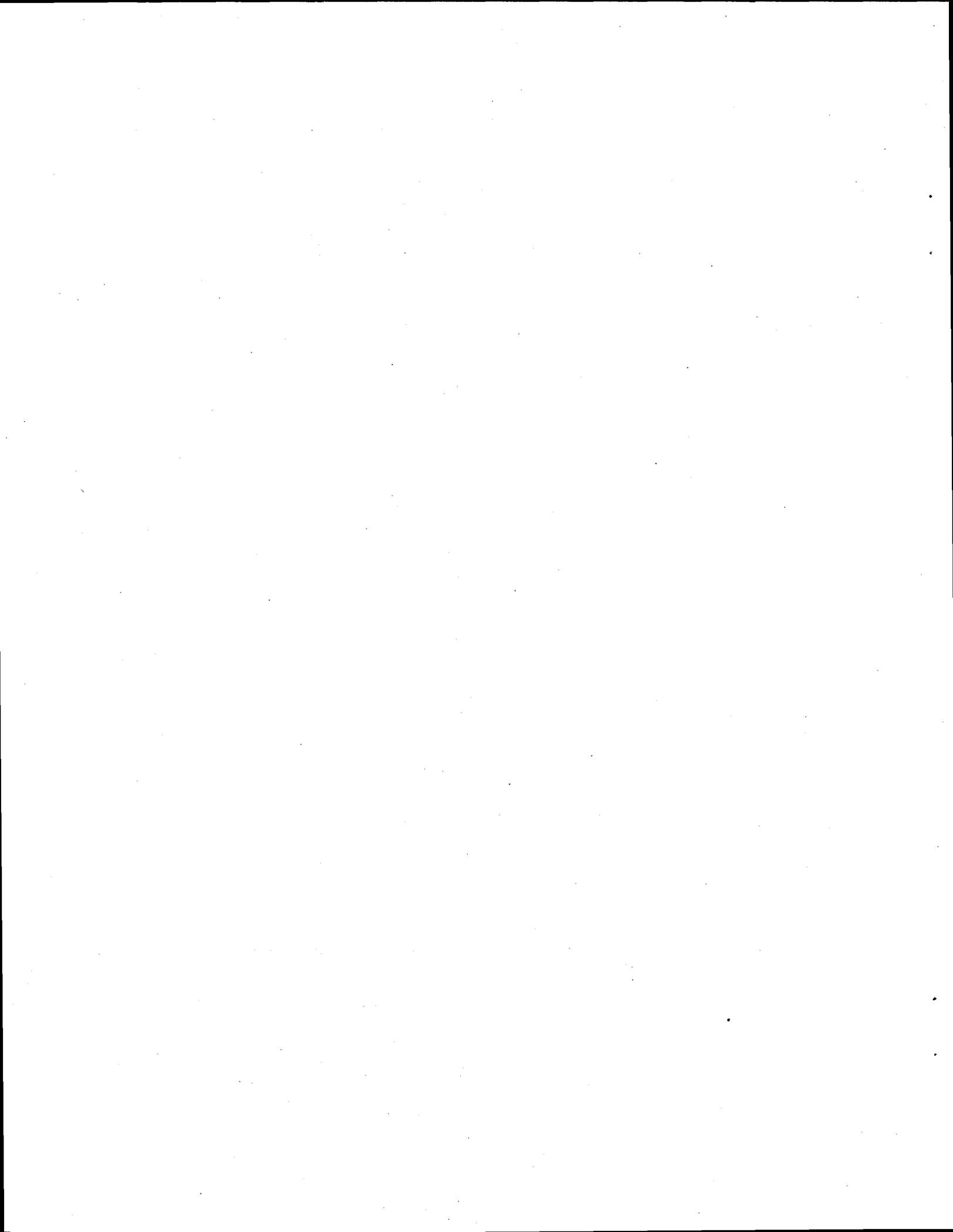
A temporal study was initiated in January 1996 in order to understand the influences seasonal temperature changes have on the vapors in the headspace of Hanford waste tanks. Three successful sampling events were conducted in FY 1996, while two additional events remain to be completed in FY 1997. A final report on the effects of temporal changes will be issued in FY 1997.

A holding time study was initiated in the fourth quarter of FY 1996. Samples were collected from tank S-102 and rushed to the laboratory for time zero analysis. The first samples were analyzed within a few hours of being taken. Additional samples will be analyzed at 1, 2, 4, 8, 16, and 32 weeks. Completion of the holding time study is scheduled for May 6, with a final report due on June 17, 1997.



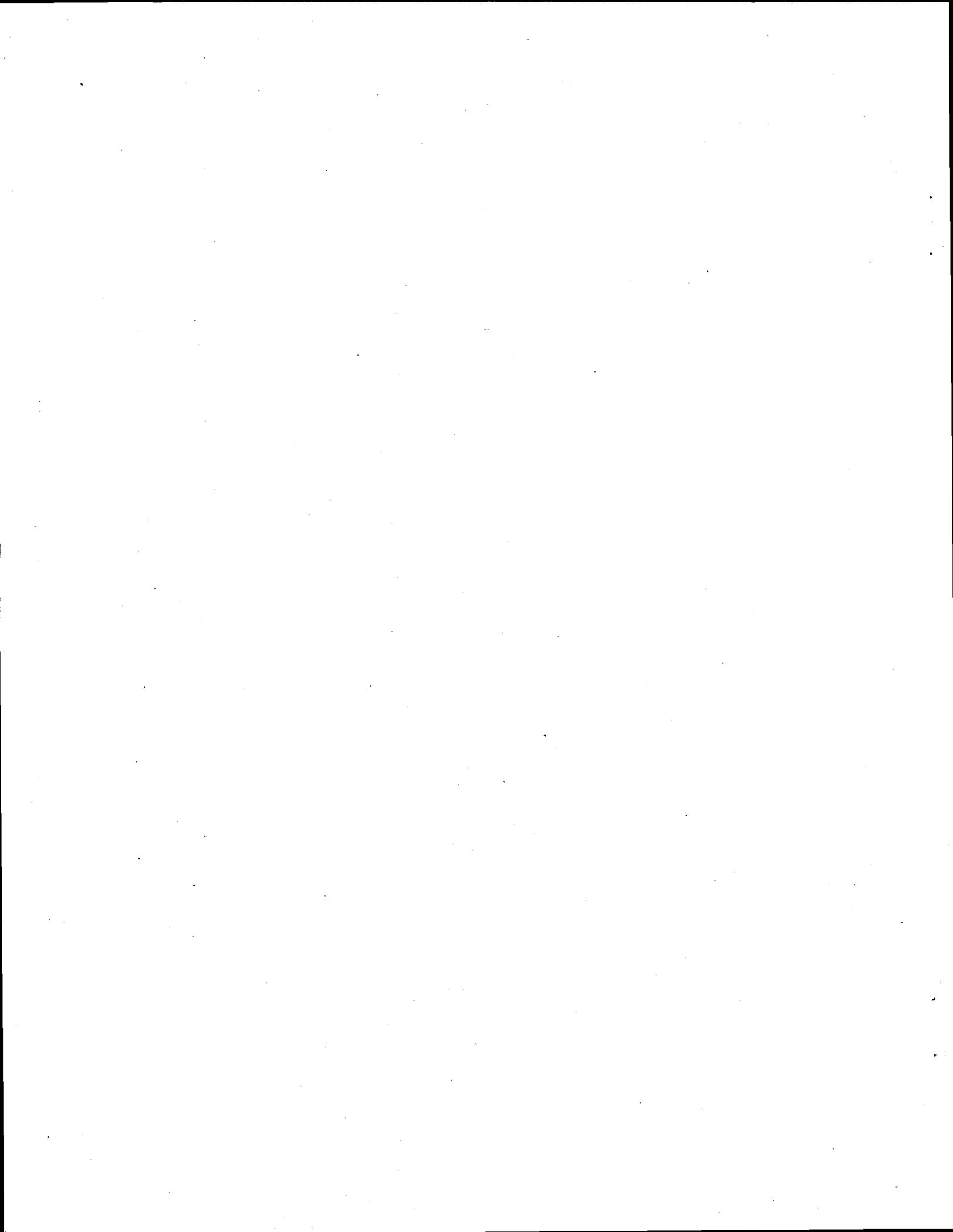
Acknowledgments

The authors wish to acknowledge the significant contributions of PNNL staff who contributed technically and otherwise to the successful completion of work in FY 1996. These people include: T.L. Burruss, T.W. Clauss, K.J. Kuhl-Klinger, J.F. Mucha, and L.E. Tooker.



Abbreviations

CAS	Chemical Abstracts Service
C _v	Concentration by volume (e.g., ppmv and ppbv)
DOE-RL	U.S. Department of Energy Richland Operations
EPA	U.S. Environmental Protection Agency
EQL	Estimated quantitation limit
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
ICV	Independent calibration verification
IS	Internal standard
ISVS	In Situ Vapor Sampling System
NIST	National Institute for Standards and Technology
OVA	Organic vapor analyzer
OVM	Organic vapor monitor
PNL	previous designation for Pacific Northwest Laboratory
PNNL	Pacific Northwest National Laboratory
ppbv, ppmv	Concentration by volume
QA	Quality Assurance
RMCS	Rotary mode core sampling
SAP	Sampling and analysis plan
SRM	Standard reference material
STP	Standard temperature and pressure (0°C and 760 torr)
SUMMA™	Passivated stainless-steel whole-air collection vessel
TAP	Toxic air pollutant
TIC	Tentatively identified compound
TNMOC	Total non-methane organic compounds
TST	Triple sorbent trap (thermal desorption method)
TVD	Tank Vapor Database
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



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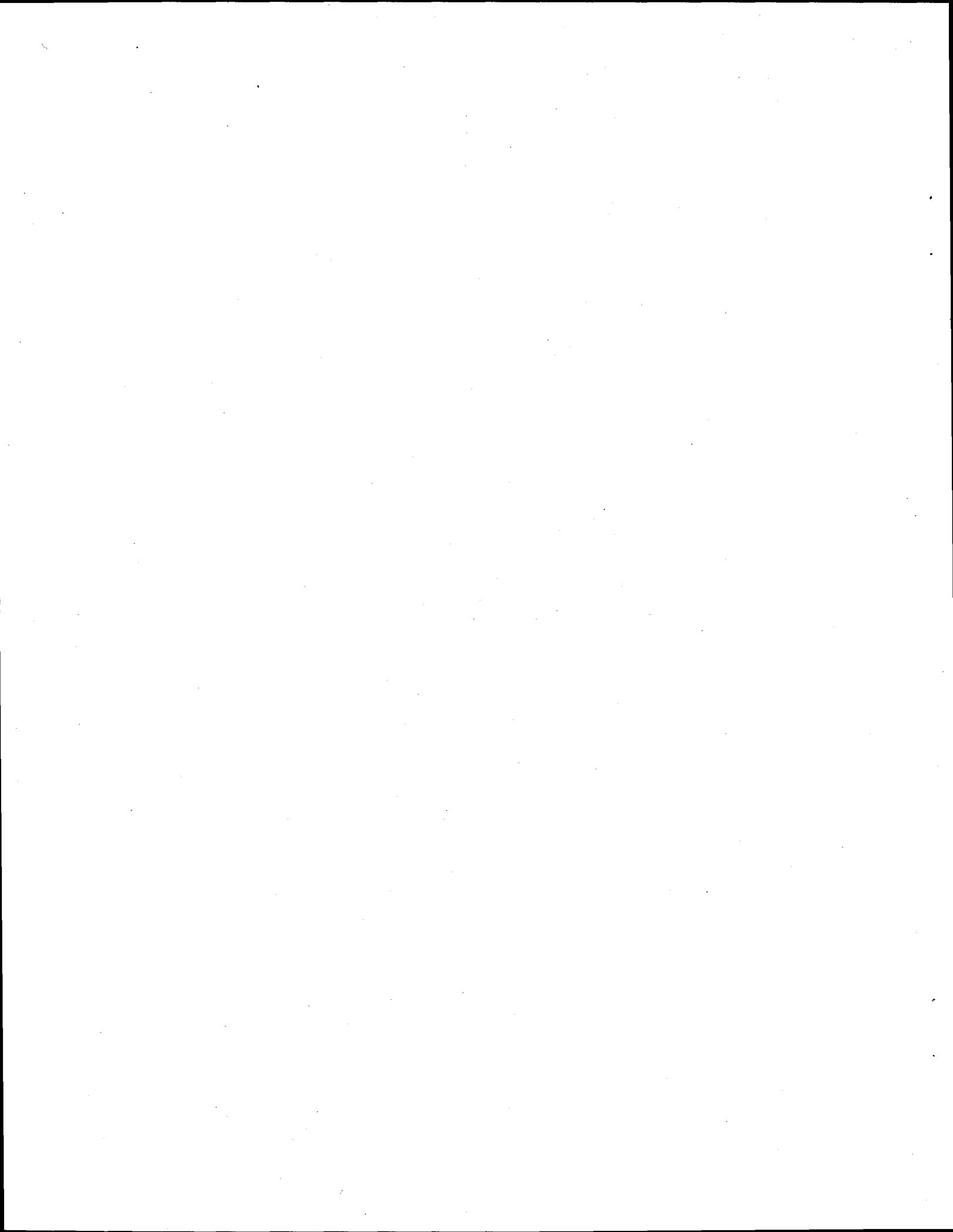
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1.0 Introduction

Westinghouse Hanford Company (WHC) was responsible for reporting the characteristics of the headspace vapors of the radioactive waste tanks at Hanford. The Pacific Northwest National Laboratory (PNNL) performed work in FY 1996 to support the characterization of headspace vapor in waste tanks at the Hanford Site. The primary scope of the project in FY 1996 was to support analyses for organic vapor (TO-12, TO-14, and TST), permanent gas, and inorganic vapor. In addition to the analytical activities, work scope in FY 1996 also included providing technical support for the vapor program, tank vapor database, and other related activities.

This annual status report contains summarized information on work completed, progress, 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). 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: KL Silvers (Project Manager, March 1996 to present), MW Ligothke (Project Manager, June 1995 to March 1996), JL Huckaby, and TL Almeida

Project Management objectives include the 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. In addition, the task included technical support of the WHC vapor project during FY 1996.

2.1 Summary of Work - FY 1996

Project staff supported the WHC tank vapor characterization project in FY 1996 by completing carry over work from FY 1995 (completed analysis and issued 11 final reports), supporting sample media preparation for 52 sample events, performing analysis on samples collect from 50 events, and issuing draft analytical data reports for 51 sample events. In addition, the vapor project is scheduled to surpass the WHC Key milestone (T24-97-138) requirements by issuing 51 final reports, three more than required by the milestone.

The vapor project also supported several key activities for the WHC Vapor Characterization Program. Two notable items are the sampling comparison study between the vapor sampling system (VSS) and the in situ vapor sampling system (ISVS) and the temporal study of tanks C-107, S-102, BY-108 and BX-104. The extensive comparison study evaluated the two sampling methods (VSS and ISVS) and provided the necessary information for the characterization project to make a switch to the ISVS sampling methodology. The switch in sampling methods provided a significant cost savings to the characterization program. The temporal studies were initiated in January 1996 and are scheduled to be complete in July 1997. The temporal study is intended to identify any differences in analyte concentrations in the vapor headspace of waste tanks as a function of seasonal heating and cooling.

Laboratory capacity was greatly increased during the fourth quarter of FY 1996. The analytical through put went from a scheduled four events per month to 10 actual events per month in both August and September. The increase in capacity was a strategic move to accommodate a large analytical work load planned in FY 1997. The ramp in laboratory the capacity was reflective of the high analytical demand in the first quarter of FY 1997. A Defense Nuclear Facility Safety Board (DNFSB) commitment requires that 18 sampling events be conducted in the month of October. This effort constitutes nearly 30% of the FY 1997 work scope. The laboratories strategic move to meet the FY 1997 work load has assured timely completion of work scope for the Vapor Characterization Program.

Other contributions made by project staff, but not included elsewhere in this report are review and approval of sampling and analysis plans before sample jobs and contracting a subject area expert for review of the sample comparison study report.

The Quality Assurance (QA) of work performed at PNNL during FY 1996 was changed as a result of implementation of the Hanford Analytical Services Quality Assurance Plan (HASQAP). The Vapor Project Quality Assurance Plan was revised to comply with the requirements of HASQAP, and procedures were updated in response to these changes. Analytical methods were qualified, and performance data were obtained. A list of the current procedures is shown in Appendix A. These changes were largely accomplished during the first half of the fiscal year.

Accompanying the scheduled implementation of HASQAP requirements for the project in FY 1996 were two quality assurance assessments performed by WHC. The first assessment, AR95-011, was performed in December 1995 to ensure compliance with the requirements defined in HASQAP and to verify completion of corrective actions associated with earlier assessment AR95-007. Two observations and four concerns were identified by the assessment team. All audit items associated with Assessment AR95-007, with the exception of two observations were determined to be complete by the auditors. The second assessment, AR96-003, was performed in June 1996 to verify completion of corrective actions associated with Assessment AR95-011. All observations and concerns associated with Assessment AR95-007 were considered closed with the exception of Observation 2. No actions or responses were required by the project as this issue was elevated to WHC Vapor Program Management for resolution.

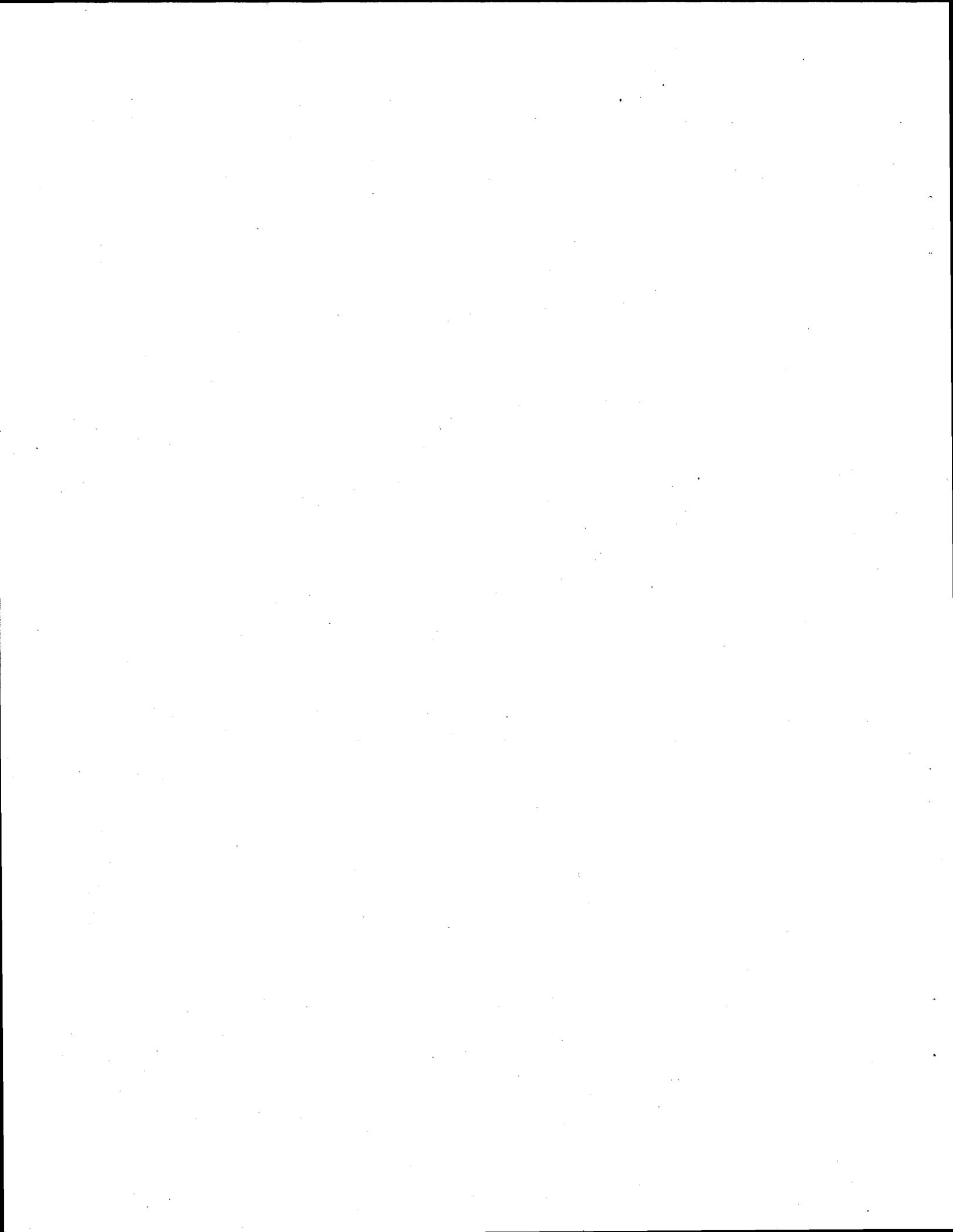
2.2 Technical Support for Vapor Characterization

PNNL supported six major Vapor Project initiatives in FY 1996 and provided broad technical support to WHC for many small issues. The six major initiatives were as follows:

- **Headspace Characterization Reports.** PNNL staff made final revisions to 23 individual tank headspace characterization reports and a summary report to satisfy Safety Initiative SI-2o and associated TPA Milestones M-40-03 and M-40-08.
- **Technical Basis Document.** PNNL technical staff wrote a tank headspace characterization technical basis document and submitted the document to WHC for review. Subsequent to delivery, WHC decided to incorporate material from this document into the Characterization Program technical basis document.
- **Validation of the In Situ Vapor Sampling (ISVS) System.** PNNL technical staff designed the comparison testing of the in situ vapor sampling (ISVS) system and the Vapor Sampling System (VSS) and prepared the final report. PNNL selected three tanks as subjects of the study, wrote the governing test plan and sampling and analysis plan (SAP), and participated in field activities. Presentations on the results of the comparison tests were given to the Chemical Reactions Sub-Technical Advisory Panel and staff from the DNFSB.
- **Study of Temporal Changes in Tank Headspace.** PNNL technical staff designed a study to determine seasonal and long-term (i.e., one year) changes in the composition of tank headspaces. PNNL selected four tanks as subjects of the study, wrote the governing test plan and SAP, and participated in initial field activities.

- **Headspace Homogeneity Study.** A study to address potential vertical and/or horizontal composition differences within tank headspaces is to be conducted in October 1996. PNNL technical staff selected three tanks to be subjects of this study, and assisted in the preparation of the governing test plan and SAP.
- **Rotary Mode Core Sampling System (RMCS) Air Permitting Support.** PNNL technical staff supported WHC air emission regulatory personnel in the revision of the RMCS portable exhauster air permitting. Tank headspace characterization data were screened for toxic air pollutants (TAPs) listed as regulated emissions in the Washington Administrative Code. All TAPs identified in the tank headspaces were entered into a spreadsheet, where a variety of statistics and calculations were performed. PNNL chemists assessed the entire list of TAPs for species that could be present in the tank headspaces at levels of regulatory concern. The resulting assessment was peer reviewed by independent scientists at PNNL, WHC, and Los Alamos National Laboratory.

In addition to these major initiatives, PNNL staff provided technical support to the WHC Vapor Program as requested throughout the year. These activities included responding to numerous requests from WHC and DOE-RL personnel for headspace characterization information, help with resolution of field sampling problems, support of the comparison of SUMMA™ canister sample TO-12 analyses with organic vapor monitors (OVMS) and organic vapor analyzers (OVAs), and a proposed reduction in the number of target analytes needed to satisfy air emission characterization requirements.



3.0 Organic Sampling and Analysis Task

Staff: JS Fruchter (Task Leader), JC Evans, BL Thomas, JL Julya, JA Edwards, KB Olsen, AV Mitroshkov, TL Almeida, OP Bredt and TG Walker

The objective of this task was to provide organic analyses of the headspace samples from the waste tanks located at the Hanford Site 200 Areas. Target organic analytes include the TO-14 analytes plus an additional 27 tank related compounds. The target analytes were detected and quantified in tank vapor samples collected in SUMMA™ canisters and/or vapor samples collected on triple sorbent traps (TSTs). A variety of other volatile and semi-volatile organic compounds were routinely identified as tentatively identified compounds (TICs) in tank vapor samples collected by these two methods. Samples collected in SUMMA™ canisters were also analyzed using the TO-12 method for total non-methane organic compound concentration, and a suite of permanent gases, including hydrogen, nitrous oxide, methane, carbon dioxide and carbon monoxide.

3.1 Sampling and Analytical Methods

3.1.1 Summary

Staff supporting the organic task of the PNNL tank vapor characterization project supported preparations for 64 tank vapor sample jobs during FY 1996. These included 19 VSS jobs, 30 ISVS jobs, seven probe cleaning tests, seven OVM jobs, one tracer test, and one holding time study. SUMMA™ canister samples from 53 of the tank samples were analyzed for permanent gases including hydrogen, carbon monoxide, carbon dioxide, nitrous oxide, and hydrogen using PNL-TVP-05. Forty-six of the tank samples were analyzed for TO-12 analyses, using procedure PNL-TVP-08. SUMMA™ canister samples from 33 of the samples were analyzed for a target list of 64 compounds that included the 39 U.S. Environmental Protection Agency (EPA) TO-14 analytes plus an additional 25 tank-specific compounds. The method used was a modified TO-14 procedure (PNL-TVP-03). In addition, TST samples from 30 tank jobs were analyzed using a thermal desorption method (PNL-TVP-10) for 61 compounds. The list of target compounds was extended to 64 compounds for TSTs and 66 compounds for TO-14 through the addition of two alcohols (methanol and ethanol) and 1,3-butadiene to the other tank-related compounds. The retention time and mass spectral characteristics of tributyl phosphate (TBP) was determined; however, the verification of calibration acceptability was not performed because the compound was not present in the continuing calibration verification. At present, it is not possible to prepare a gas standard from this material. This new target list was used on the tanks processed at the end of FY 1996.

3.1.2 Technical Procedures

Although no entirely new analytical procedures were developed in FY 1996, several of the procedures were improved.

Procedures Improved: In order to comply with HASQAP, method validation and instrument detection limit (IDL) studies were performed for the permanent gas, TO-12, TO-14, and TST methods. Work on revising the TST method (PNL-TVP-10), the TO-14 method (PNL-TVP-03), the permanent gas method (PNL-TVP-05), and the TO-12 method (PNL-TVP-08) was completed. The

project QA plan was also completed. In addition, vapor organic task staff were trained to the Quality Assurance Plan, ETD-002.

The feasibility of calibrating the TST method for TBP was explored. It appears that using a direct injection method onto the TSTs will be successful.

A comparison study of initial calibrations using available TO-14 standards was performed. The two Scott standards (different lots) agreed well with each other for all 39 compounds. However, they did not agree well with the Matheson standard for six compounds. None of these six compounds are target analytes, nor have they been found in any of the tank samples.

Permeation tube standards for ethanol and methanol were received, and new standards were prepared. As a result, these compounds have now been added to the target list.

Since the initial performance studies were performed early in the year, new commercially prepared TO-14 standards were obtained from Air Liquide and Scott Marin, respectively. All subsequent calibrations used during the remainder of the year routinely used the Scott Marin standard as an independent calibration verification (ICV), with specific performance criteria required for the acceptance of the calibration. An independently prepared permeation tube standard was also included in each ICV. Agreement between standards was commonly obtained for all compounds on the list at the 25% level.

3.1.3 New Equipment/Facilities/Software

The new gas chromatography/mass spectrometry (GC/MS) UNIX-based computer data system was received from Hewlett Packard (HP) and installed in the laboratory. The new system employs three workstation terminals, greatly improving data throughput. The report generation software was upgraded to provide better QA reports.

An office in the 326 Building for the project analysts was obtained and occupied. The office provides support for sample and report preparation, as well as record storage.

The TST GC/MS system was upgraded with a new source and multiplier. The order for the thermal desorber unit for the second TST system was placed and received. The second TST system has been set up using a GC/MS donated by another project. It is being used to develop procedures for the target list and as a backup to the first system.

Networking of the laboratory was completed in mid-year with full communication established between three Unix workstations, six GC computers, and two Macintosh systems used for report preparation. External communications outside the laboratory are provided through the Hanford LAN backbone.

An additional 60 SUMMA™ canisters were purchased, bringing the total to 330.

3.1.4 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 were cleaned according to Technical Procedure PNL-TVP-02^(a) and verified contaminant free according to Technical Procedure PNL-TVP-08^(a). The cleaning procedure used an EnTech 7000 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 was filled a final time with purified humid air for analysis by EPA compendium Method TO-12, which is also found in Technical Procedure PNL-TVP-08. If the canister was verified as clean and free of TO-12 contaminants to a level of 5 parts per billion by volume (ppbv), the canister was 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 was measured to determine if any leakage had occurred. If the vacuum had remained constant during storage, the canisters were prehumidified with 100 µL of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days were re-evacuated and rehumidified before use. If stored more than 60 days, the canisters were recleaned and validated before use.

Triple Sorbent Traps: Samples were collected on Supelco 300 graphite based TSTs. Before field deployment, each trap was heated to 380°C under inert gas flow for a minimum of 60 min. Tubes were prepared in batches with each tank sampling job constituting one batch. One tube was selected from each batch and run immediately to verify cleanliness. All remaining tubes in the batch received equal amounts of three surrogate compounds (hexafluorobenzene, toluene-d8, and bromobenzene-d5). One tube per batch was run immediately to verify successful addition of surrogate spikes to that batch. Tubes were then placed in individually labeled plastic shipping tubes (Supelco TD³), which were sealed with gasketed end caps, thus providing a rugged, headspace-free shipping and storage medium. Several tubes from each batch, containing surrogates, were archived and stored for use as daily calibration standards. As a precautionary measure, sample tubes were kept in refrigerated storage before and after sampling.

3.1.5 Sample Analyses

Permanent Gases: The SUMMA™ canister samples were analyzed for permanent gases according to PNL-TVP-05^(b), with the exceptions listed in the following text and in the Quality Assurance/Quality Control section of this report. This method was developed in-house to analyze permanent gases defined as hydrogen (H₂), carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), and nitrous oxide (N₂O), by gas chromatograph/thermal conductivity detection (GC/TCD). Aliquots of sampled air were drawn directly from each canister into a 5-mL gas-tight syringe and injected into an HP 5890 GC/TCD fitted with a loop injector valve and a column switching valve.

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

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

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

An aliquot of 5 mL was used so that the 1.0-mL injection loop was completely purged with sample air, ensuring that no dilution of the sample took place within the injection loop. One set of GC conditions was used to analyze for CO, CO₂, N₂O, and CH₄ using Helium (He) as the carrier gas. A second GC analysis was performed for H₂, 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 were blended from commercially prepared and certified standards for each of the analytes. The instrument was calibrated for CO, CO₂, N₂O, and CH₄ over a range of 25 to 700 parts per million by volume (ppmv) using standards at five different concentrations and He as a carrier gas. A similar procedure was followed for H₂, except the carrier gas was changed to N₂. The concentration of individual compounds were determined by applying the average response factors from the calibration curve to the peak area responses for the analytes.

Total Non-Methane Organic Compounds: The SUMMA™ canister samples were analyzed according to PNNL Technical Procedure PNNL-TVP-08, which is similar to U.S. Environmental Protection Agency (EPA) compendium Method TO-12. The method detection limits in the sub mg/m³ were required to determine total non-methane organic compounds (TNMOC) concentration in the tank samples.

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

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

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

The TNMOC was calibrated by using propane as the calibration standard and using that response factor as an external standard method. The instrument calibration mixture for the PNL-TVP-08 analysis consisted of National Institute for Standards and Technology (NIST) 99.999% propane analyzed using a 10-point, multilevel, average response factor method for calibration.

Before the tank samples were analyzed, a diagnostic check was performed on the GC/FID instrument by running a system cleanliness procedure and an instrument continuing calibration as described in PNL-TVP-08. First, two blank volumes of Aadco purified air were analyzed to check the cleanliness of the system. This demonstrated through the analysis of a zero-air blank that the

level of interference was acceptable in the analytical system. Second, an instrument continuing calibration run was made using 100-mL UHP propane analyzed using the response factor as an external standard method, followed by one blank volume of Aadco air.

Volatile Organic Analytes by TO-14: The SUMMA™ canister sample was analyzed according to procedure PNL-TVP-03^(a), which is a modified version of EPA compendium Method TO-14. The method uses EnTech 7000 cryoconcentration systems interfaced with a 5972 HP benchtop GC/MS. The EnTech concentrator was 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 was measured and analyzed from the tank headspace. The organic components in the sampled air were separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm internal diameter with 3- μ m film thickness. The GC oven was programmed to run a temperature gradient beginning at 40°C, hold for 5 minutes, and ramp at 4°C per minute to a final temperature of 260°C, with a 5-minute hold. Twenty-four hours before the analysis, the SUMMA™ canister samples were pressurized with purified air (Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The starting pressure was first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level exactly twice the original pressure. For example, if the canister had a starting pressure of 740 torr, it was pressurized to 1480 torr. This dilution was an effort to improve the precision of the analysis. The sample dilution was taken into account when calculating the analysis results.

The instrument calibration mixture for the PNL-TVP-03 analysis consisted of the standard 39 organic analytes with an additional 27 tank-related compounds. Together, these 66 compounds that are directly quantified in this analysis make up the target analyte list (these 66 compounds are referred to as target analytes). The calibration mixture was prepared by blending a commercially prepared 39-compound TO-14 calibration mixture with a 27-compound mixture created using a Kin-Tek® permeation-tube standard generation system. The operation of the permeation-tube system follows the method detailed in procedure PNL-TVP-03. The standard calibration mix was analyzed using six aliquot sizes ranging from 10 mL to 450 mL, and a response factor for each compound was calculated. The GC/MS response for these compounds had been previously determined to be linearly related to concentration. Performance-based detection limits for the target analytes were used for establishing quantitation limits. Nominal detection limits of 5 ppbv or less were typical.

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 procedure 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 the calibration mixture described above. 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, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard

^(a) Pacific Northwest National Laboratory. 8/96. *Speciation and Quantification of Organic Vapors in Hanford Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-03 (Rev. 2), PNNL Technical Procedure, Richland, Washington.

concentration (in ppbv) to the IS concentration. Once it was determined that the relative response was linear with increasing concentration, an average response factor was calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks were analyzed before and after calibration standards and tank-headspace samples were analyzed.

Volatile and Semi-Volatile Organic Analytes by Sorbent Trapping: The tubes were analyzed according to Technical Procedure PNL-TVP-10^(a). 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 were transferred to a Dynatherm ACEM 900 thermal desorber unit for analysis. The trap on the ACEM 900 was then desorbed by ballistic heating to 350°C with the sample then transferred to a smaller focusing trap. A nominal 10:1 split was 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 was 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 was transferred to a long, thin (0.4 mm ID) 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 He flow rate compatible with the column and MS interface (1.2 mL/min). The focusing trap was ballistically heated to thermally desorb components onto a capillary GC column. The column was subsequently temperature programmed to separate the method analytes, which were then detected by MS.

The instrument calibration mixture for the TST analysis consisted of the standard 37 organic analytes with an additional 27 tank-related compounds. Two compounds typically found on the TO-14 list were not included—bromomethane and benzyl chloride. Together, these 64 compounds that are directly quantified in this analysis make up the target analyte list (these 64 compounds will be referred to as target analytes). The calibration mixture was 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 were measured by pressure difference on a SUMMA™ canister of known volume. The GC/MS response for these compounds had been previously determined to be linearly related to concentration. Performance-based detection limits for the target analytes have been developed and used routinely to provide quantitation. Nominal IDLs of 5 parts per billion by volume (ppbv) or better were typical for 200-mL tank vapor samples.

Before a tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running a full auto tune, as described in procedure PNL-TVP-10. Upon satisfactory

^(a) Pacific Northwest National Laboratory. 2/96. *Determination of Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using Triple Sorbent Trap Sampling and Gas Chromatograph-Mass Spectrometer Analysis*, PNL-TVP-10 (Rev. 2), PNNL Technical Procedure, Richland, Washington.

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 64 compounds. A gas mixture containing difluorobenzene, chlorobenzene- d_5 , and 1,4-bromofluorobenzene was used as an IS for all calibration standard and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. A continuing calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it was determined that the relative response was linear with increasing concentration, an average response factor was calculated for each target analyte and used to determine the concentration of target compounds in each sample.

3.1.6 Sample Calculations and Reviews

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 was reported as the method detection limit based on Rev. 2 of the procedure. 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 fell within $\pm 25\%$ of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. An N_2 reagent blank, an ambient-air sample collected ~ 10 m upwind of the tank being sampled, and the ambient air collected through the VSS were used to determine the potential for analyte interferences in the samples.

Volatile Organic (TO-14) 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 procedure PNL-TVP-03. The conversion from ppbv to mg/m^3 assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

The TICs were 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 were tentatively identified and quantitatively estimated. This was 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 was estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration in mg/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 were 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 were 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 2 to account for the dilution step.

Triple Sorbent Trap 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 procedure PNL-TVP-10. The conversion from ppbv to mg/m³ assumed 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 were determined by mass-spectral interpretation and comparison of the spectra with the EPA/NIST and Wiley Libraries, which are a part of the HP 5971/5972 instrument operating system. Chromatographic peaks with an area count greater than or equal to one-tenth of the total area count of the nearest eluting IS were tentatively identified and quantitatively estimated. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

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

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

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

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

The IS concentrations were 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.

3.1.7 Data Reports and Technical Papers

A total of 42 data packages for the analyses were issued, including 15 screening reports and 27 full characterization reports. All data packages and reports required to meet the project milestones were submitted on time.

The following manuscript was prepared and published:

Goheen, S. C., B. D. McVeety, T. W. Clauss, R. B. Lucke, M. W. Ligothke, J. A. Edwards and J. S. Fruchter (1996) "Organic Analysis of the Headspace of Hanford Waste Tank 241-C-103" , *J. Radioanalytical and Nucl. Chem.*, v 207, No. 1, pp. 81-91.

3.2 Method Validation and Special Studies

Side-by-side vapor sampling method comparison tests were supported for two repeats of three separate tanks. A statistically valid approach and a tank SAP were prepared to compare the new ISVS sample, cart-based sampling system, to the established heated-probe VSS, truck-based sampling system. Sample media were prepared, and samples were analyzed for tanks C-107, S-102, and BY-108.

Analyses of TST samples from the Bundle Study were also completed. The results showed low levels of contamination from the tape used to prepare the ISVS bundles for sampling. These results are discussed in Section 3.4.

3.3 Quality Assurance

The laboratory portion of the WHC Assessment AR95-011 was completed. A corrective action plan to respond to the observations and concerns was developed, and implementation was completed. All observations and concerns were resolved and closed.

The procedure for determination of Permanent Gases, PNL-TVP-05, was revised twice to incorporate HASQAP requirements, clarify the requirements for control charting, and redefine the estimated quantitation limits for the method.

The procedure for speciation and quantification of organic vapors using SUMMA™ passivated canister sampling (PNL-TVP-03) was revised twice to incorporate HASQAP requirements and method qualification information, and method qualification information for a second analytical system.

The procedure for determining volatile organic compounds using TSTs, PNL-TVP-10, was revised twice to incorporate HASQAP requirements and method qualification information.

3.4 Major Problem Areas and Resolution

Blank samples from the ISVS from tanks C-107 and BY-108 contain large numbers of peaks in the chromatograms. Compounds identified include alkanes, cycloalkanes, alcohols, and a chlorofluorocarbon. The hydrocarbons and alcohols appear to originate from the tape being used to hold together the sample bundle. The source of the chlorofluorocarbon has not yet been determined. These contaminants were also seen in the samples from these two tanks.

SUMMA™ canister blank samples from the ISVS from tank C-107 contained large numbers of peaks in the chromatograms, similar to those observed earlier in the TST analysis of this tank. The quantities present in the SUMMA™ canisters appear to be about one third the amount seen in the TST blanks. Compounds identified include alkanes, cycloalkanes, alcohols, and a chlorofluorocarbon.

Initial TO-14 analyses of S-102 and BY-108 showed that certain constituents, particularly n-butanol, were present in the samples at concentrations higher than the calibration studies. The TO-14 procedure requires that in these circumstances, the samples be diluted and rerun until all analytes can be analyzed at concentrations below the highest calibration standard. The S-102 samples had to be diluted and rerun once. The BY-108 samples required two dilutions and reruns to achieve this objective.

The EnTek 7000 cryoconcentrator for TO-14 System 1 began to malfunction, resulting in an inability to achieve calibration objectives for the TO-14 method. The problem was traced to water management in the system using the micro-scale purge and trap method. The problem was ultimately corrected, but resulted in a 10-week downtime for the TO-14 method.

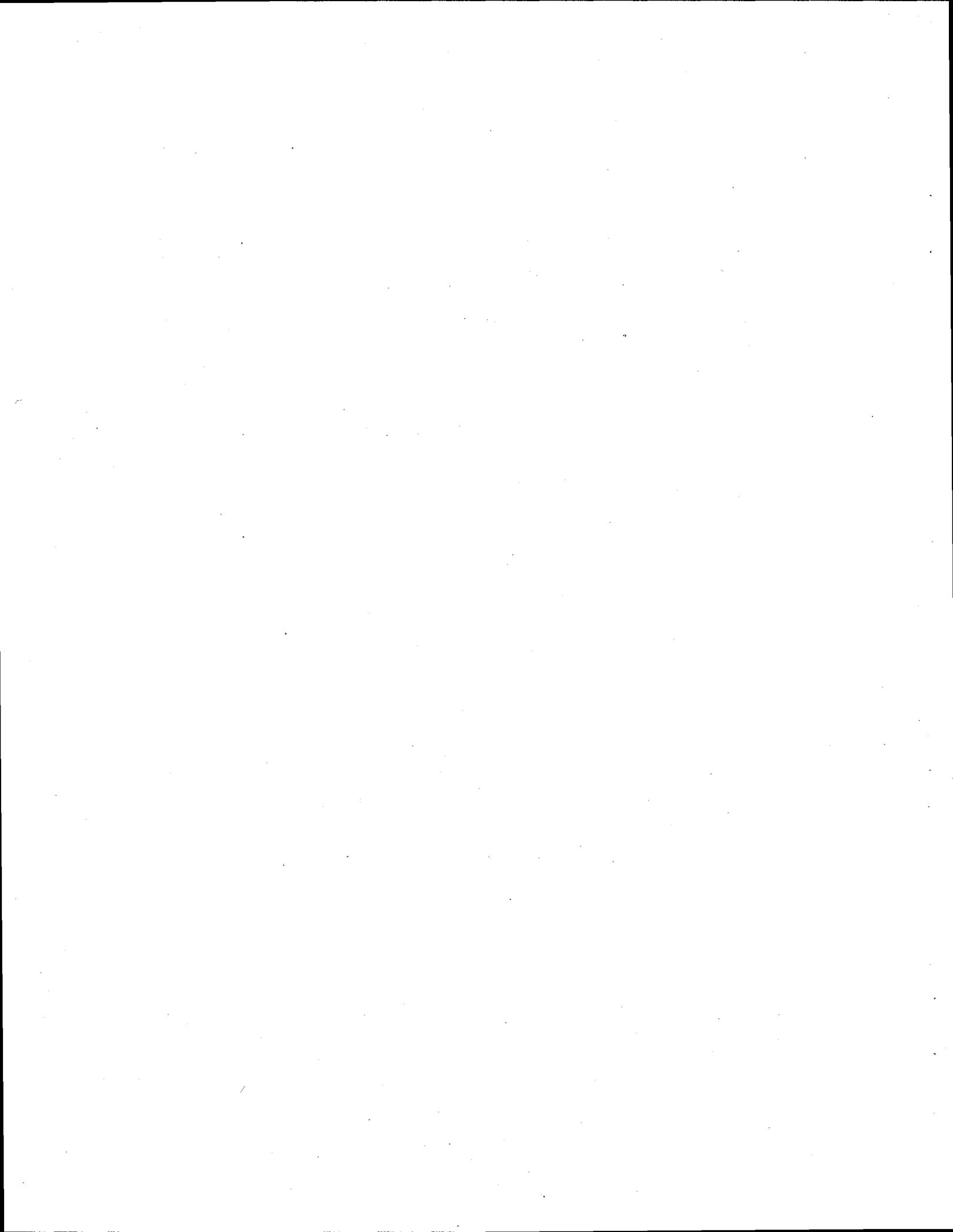
The EnTek 7000 for TO-14 System 2 was returned to the factory for reconditioning. After its return, an EnTek factory representative visited the vapor laboratory on July 1 and 2. As a result, the problems with the EnTek 7000 cryoconcentrator on System 2 were solved. The project now has two operational TO-14 systems.

Because of problems with the EnTek systems, an alternate type of cryoconcentrator, manufactured by NuTek, was tried. A NuTek system, which had been purchased by the project in FY 1995, was set up in the laboratory. A service representative from NuTek visited our laboratory and assisted with the set up. Unfortunately, tests with the NuTek cryoconcentrator indicated that this device will not be suitable for tank headspace samples, because it cannot handle polar compounds adequately and exhibited serious water management problems with the tank headspace samples. Therefore, it will be necessary to keep the EnTek concentrators fully functional.

The appearance of measurable tritium in silica gel traps from two tank samples caused WHC to label the SUMMA™ canisters from these sample jobs as radioactive. This caused a minor delay at the vapor laboratory for additional PNNL RadCon clearance. The problem was solved, and low-level tritium contamination should not be a problem in the future.

The SUMMA™ canister samples from tank C-202 were held up in a radiation zone because WHC had detected beta radiation on the second high-efficiency particulate air (HEPA) filter for this sample. The vapor inside the canister was transferred through a series of filters to a second SUMMA™ canister. No radioactivity was detected on the filters, and the sample was cleared by PNNL Radiation Control. The C-202 sample was transferred to the vapor laboratory and was subsequently analyzed.

The QA assessment of the PNNL Vapor Project (AR95-011) resulted in two observations and one concern involving the organic task. These observations and concerns were resolved by conducting method qualifications and subsequent procedure revisions. This assessment was closed by the WHC assessment team.



4.0 Inorganic Sampling and Analysis Task

Staff: KH Pool, SO Slate, LMP Thomas, GW Dennis, KP Schielke, and TL Almeida

The objective of the inorganic task was to provide technical support and inorganic analytical chemistry for waste tank headspace samples. Support was provided for both VSS and ISVS sampling events. 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

4.1.1 Summary

Staff supporting the inorganic task of the PNNL tank vapor characterization project supported preparations of all 50 vapor sample jobs scheduled in FY 1996, analyzed sorbent trap data from 49 jobs, and completed 49 report chapters. Support was also provided for the effort to complete late-FY 1995 sample jobs and resolve the backlog of reports from sample jobs performed in FY 1995; report input was provided for 10 such sample jobs. In FY 1996, 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 SAPs for any vapor jobs performed in FY 1996.

4.1.2 Technical Procedures

Procedures PNL-TVP-09 Rev. 2 and PNL-TVP-07 Rev. 2 were prepared and implemented in December 1995. These procedures guide sorbent trap preparations and control for sampling and analyses.

4.1.3 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 connected in series using Perfluoroalkoxy 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 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. Trip and/or field blank 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 1995. The two-section sorbent traps used for vapor sampling included: 500 mg + 250 mg carbon beads impregnated with sulfuric acid (NH_3), 400 mg + 200 mg of a zeolite impregnated with triethanolamine (NO_2 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.

4.1.4 Sample Analyses

All sample analyses were performed following 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 NH_3 , NO_2 , 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 NO_2 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 (Claus et al. 1994, Ligothke et. al. 1994).

4.1.5 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 NH_3 equals

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

This calculational method produces concentration results that were slightly conservative (greater than actual) because the volume of water vapor in the sample stream was 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 was 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 technical reviewer before final input was provided for the data reports. Original and confirming work is documented.

4.1.6 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 1996 samples jobs and for 10 FY 1995 sample jobs. Staff also contributed to a few technical abstracts for conferences and project reviews.

4.2 Quality Assurance

The laboratory portion of the WHC Assessment AR95-011 was completed. A corrective action plan to respond to the observations and concerns was developed, and implementation was completed. All observations and concerns were resolved and closed.

Calibration verification of the Hi/Lo trip thermometers was performed and documented.

An Interim Change Notice was issued for the shipping, receiving, and handling procedure (PNL-TVP-07) to correct inconsistent temperature requirements.

Analytical work was performed according to quality levels identified in the project QA plan and several PNNL documents. The samples were analyzed following PNNL Impact Level II requirements. The PNNL documents include PNL-MA-70 (Part 3), PNL-ALO-212, PNL-ALO-226, MCS-046, and ETD-002. A summary of the analysis procedures and limits for the target inorganic compounds is provided in Table 4.1. 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 objective assessment by Osborne et al. (1994). The table shows the estimated quantitation limit (EQL) for each of the target analytes using current procedures with a vapor-sample volume of 1.86 L and a desorption-solution volume of 3 mL (10 mL for NH₃).

Table 4.1. Analytical Procedures, Quantification Limits, and Notification Levels for Selected Inorganic Analytes^(a)

Analyte	Formula	Procedure	EQL ^(b) (μ g)	EQL ^(b) (ppmv)	Notification Level ^(c) (ppmv)
Ammonia	NH ₃	PNL-ALO-226	1.0	0.71	≥ 150
Nitrogen Dioxide	NO ₂	PNL-ALO-212	0.3	0.16	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.3	0.16	≥ 50
Mass (water) ^(d)	n/a	PNL-TVP-09	0.6 mg	0.3 mg/L	n/a

(a) Analytical precision and accuracy targets for results in the expected ranges equal \pm 25% and 70 to 130%, respectively (Osborne et al. 1995).

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

(c) As per Table 7-1 in Osborne et al. (1995). Notification levels require verbal and written reports to WHC on completion of preliminary analyses.

(d) The vapor-mass concentration, thought to be largely water vapor, is determined gravimetrically. n/a = not applicable.

The accuracy of 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 was estimated to be \pm 5% relative, independent of concentration at 1 μ g/mL or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Working standards were traceable to NIST standard reference material (SRM) by using an independent calibration verification standard, which was certified to be NIST-traceable. Nitrite analyses (for NO₂ and NO) were 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 was $\pm 5\%$ relative. The accuracy of measurements of sample mass was 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, was determined for each sample job and was typically less than ± 1 mg per 5-trap sorbent train.

4.3 Accomplishments

Laboratory support activities were, in general, completed on schedule. No sample sets were backlogged, and the backlog of report input from FY 1995 was resolved. Sample analyses from FY 1996 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 1996 included the following:

1. Procurements were made, and the required analytical capabilities were maintained throughout the year (completed on schedule 9/30/96).
2. Revised technical procedures were issued for sorbent trap preparation and control for sampling and analysis (12/95).
3. All report input was completed for FY 1995 sample jobs.
4. All analyses were completed for FY 1996 samples (9/30/96). All report input was completed for FY 1996 sample jobs (completed 10/31/96).

4.4 Major Problem Areas and Resolution

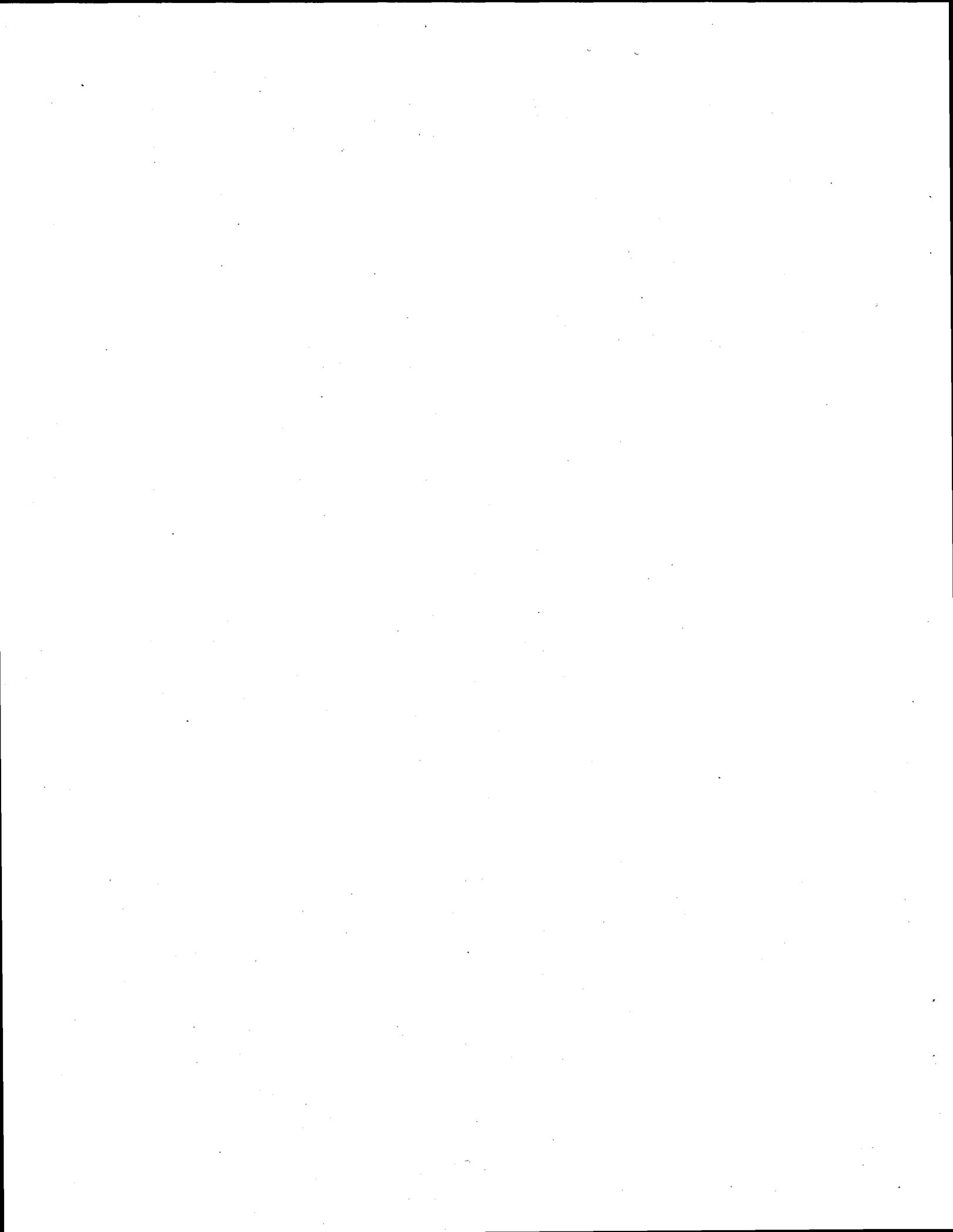
The QA assessment of the PNNL Vapor Project (AR95-011) resulted in two concerns involving the inorganic task. These concerns were resolved by procedural changes and calibration verification of trip thermometers. This assessment was closed by the WHC assessment team.

5.0 Waste Tank Vapor Data Reports

Staff: B.M. Thornton (Task Lead), D.S. Sklarew, and R.E. Schrempf

The analytical results of samples from the headspaces of waste tanks for jobs performed in FY 1995 and FY 1996 were reported in FY 1996. A complete list of the tanks analyzed and report issuance dates is provided in Appendix B. Draft reports for 10 sample jobs from FY 1995 were completed between October 1995 and January 1996. Final reports for 11 sample jobs from FY 1995 were completed in May 1996. Draft reports from 40 sample jobs from FY 1996 were completed in FY 1996. Final reports for 19 sample jobs from FY 1996 were completed in FY 1996. The remaining 21 final reports for sample jobs from FY 1996 will be completed by November 30, 1996. Draft and final reports for 10 sample jobs completed late in FY 1996 will be completed in FY 1997.

Final reports for FY 1996 sample jobs were not required to go through the formal clearance process, which required WHC and DOE-RL reviews and signatures. These FY 1996 reports were released via the PNNL Information Release process, which requires the signatures of the Author, Peer Reviewer, Editor, Project Manager, and Line Management. These documents were also reviewed and signed by the project Quality Engineer before issuance as final reports.



6.0 Waste Tank Vapor Database

Staff: CA Simonen (Task Leader), JL Huckaby, DS Sklarew, KB Walters, JA Glissmeyer, and MB Birn

Information in the Tank Vapor Database (TVD) is being used to characterize the waste in the single-shell tanks at the Hanford Site and to help make decisions on worker safety issues. The major objectives of the TVD team in FY 1996 were to load and verify data about the vapor phase of the tank wastes, to load these data within 7 calendar days from the date of issue of the final report, to support the Tank Waste Information System (TWINS2) staff in providing accessibility on the WEB, to revise and complete C-103 data, to add the capability to include field monitoring data and flammability results, to add data qualifiers, and to add holding time information. Other revisions were also made to the database structure to provide or clarify information. These objectives were successfully met in FY 1996.

6.1 Introduction

The purpose of the TVD is to store vapor data from the single-shell tanks at the Hanford Site; specifically, 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. The main objective of the TVD team in FY 1996 was to load and verify published data about the vapor phase of the tanks.

6.1.1 History of the TVD

In 1993, the WHC manager of the Tank Vapor program requested that PNNL develop extensive database capabilities to support the work being done. 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, the database was restructured and data for 33 tanks were loaded.

6.1.2 The Function of the TVD at Hanford

The TVD fits into the larger picture of information management in two ways: through the TWINS2 on the WEB and as a separate database. TWINS2 provides access to a vast array of data on the solid, liquid, and vapor phases of waste stored in the Hanford Site tanks. The data that are accessible through TWINS2 are actually stored on separate databases; two of these databases are the Tank Characterization Database and the TVD. The Tank Characterization Database contains the solid and liquid data from the Hanford Site tanks. TWINS2 provides a convenient interface in allowing the user to see both sets of data without having to learn the different data structures. The TVD can also be used as a stand-alone database and accessed through commercial front-end software, such as DataPrism.

6.1.3 Sparc1000 Server

In FY 1994, the TVD team purchased the Sparc1000 server labeled "Pygar." In FY 1995, the vapor database was moved to the new server, which involved three basic changes. First, the new server was significantly upgraded from a Sparc2 to a Sparc1000. Second, the operating system was upgraded from Sun O/S to Solaris 2.4. Third, the database engine was upgraded from Sybase Version

4.9.2 to Sybase System 10.0.2.1. This move to the new server allows the user to retrieve and manipulate data more quickly. It also allows the database administrator to perform administrative functions faster and more efficiently. An enhanced schedule of data backups improves the reliability of retrieving lost or corrupted data. Because more disk space is available, the data structure was 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.

6.2 Database Procedures

6.2.1 Data Loading

Data are loaded from published reports. Where possible, the information in the reports is sent to the TVD staff in Excel spreadsheets, which reduces the possibility of data entry errors.

The Chemical Abstract Services (CAS) number and other chemical information are extracted from an ASCII file sent by the library and transferred by a Visual Basic program to the appropriate fields in an Excel spreadsheet. These items are properly formatted before being transferred to the appropriate TVD chemical tables.

To assist in verifying the data, a Visual Basic program is used 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.

6.2.2 Reference Data for Easy Access

The complete reference citation for the data reports is stored to provide the user with the context of the data (such as the laboratory reports and GC runs). The information is entered through a user-friendly input screen created in Access.

6.2.3 CAS Numbers and Unique Identifiers

When analyzing the tank vapor samples, the laboratories occasionally list chemicals that do 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. 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 created using a systematic approach that can be replicated by others who need to add data to the TVD.

6.2.4 Chemical Categorization

To assist users in looking at the chemicals contained in the vapor phase of the tanks, a data field contains the group (such as alkanes, alkenes) to which the chemical constituent belongs. This information is pulled from a variety of reference sources and entered using an Excel and Visual Basic program, which helps to automate the data loading process. As the TWINS2 interface on WEB is under development, this will be accessible to WEB users in the future.

6.2.5 Registered Trademarks Used

Access, Microsoft Corporation, Redmond, Washington.
DataPrism, Brio Technology, Mountain View, California.
Excel, Microsoft Corporation, Redmond, Washington.
Sybase, Sybase, Inc., Emeryville, California.
Visual Basic, Microsoft Corporation, Redmond, Washington.

6.3 FY 1996 Accomplishments

6.3.1 Loading and Verifying Sample, Analysis, and Chemical Data

Automated loading and verification techniques were used for vapor sampling data for 31 tanks added to the TVD. Of these tanks, three (BY-108, C-107, and S-102) were selected for a comparison of the different sampling systems (VSS and ISVS with and without HEPA filtration) for each sampling device. Consequently, the number of results loaded for these three tanks increased dramatically. The total number of tanks with data loaded in the database is now 64 (see Appendix C), with approximately 40,000 result records.

In mid-FY 1996, a new data loading requirement was put into place. To meet TPA Milestone M-44, analytical data must be loaded into the database within 7 calendar days from the time the final report is issued. This goal has been met consistently.

When the new database capability of including field monitoring data was completed in September, results for 60 tanks were loaded (see Appendix D).

6.3.2 Improved Data Accessibility

As the TWINS2 staff has made the development version of the new enhancements to the WEB interface available, the TVD team has reviewed the changes and the impact on the vapor data. Input was provided to the TWINS2 team that enhanced the communications aspects of the interface, and modifications were made to accommodate these changes. The team helped familiarize all Vapor staff with the capabilities of TWINS2 and its accessibility on the WEB. Currently, users can access all the vapor and field monitoring results, data qualifiers list, sampling data, and references. In FY 1997, more of the current tables will become visible, such as the chemical synonyms and the chemical classifications.

6.3.3 C-103 Data Revision

Because data from tank 241-C-103 was the first to be entered into the TVD, different conventions were originally used for these data than for those of the other tanks. Therefore, these data were revised and other C-103 data were added. In particular, C-103 data for sample jobs 4, 5, 6, 6b, and 7a were added and data for sample job 7b were revised. A letter report written by J. L. Huckaby, "Technical Considerations for Inclusion of Tank 241-C-103 Headspace Characterization Data into the Tank Vapor Database", addressed these revisions and additions. After data entry, these data were reviewed on the test database before being transferred to the tank vapor production database and TWINS2.

6.3.4 Revisions to the Database Structure

The structure of the data model (see Appendices E and F) was again revised in FY 1996 to reflect the information that was provided by the laboratories and to make it more useful in the long term.

Tables relating to field monitoring data and flammability results were added to the database. These were Monitoring Data, Monitoring Results, Flammability Data, and Flammability Results.

Single- or combined-letter flags were added to the TVD as data qualifiers. A table (see Appendix G) was created to list and define eight data qualifiers that indicate noteworthy aspects of sample results. For example, "U" indicates that the compound is below the detection limit and "JN" indicates a TIC. This new data qualifier field includes the information which were in two fields that were replaced: the level of identification and level of quantification.

The distinction between sample device and sampling method was clarified by adding the sampling device field and populating both fields appropriately.

Fields for analysis date, elapsed hold time, holding time, and basis of holding time were added to help the user determine whether holding time requirements were met.

Tables relating to meteorological data were deleted because they were not needed. These tables include Sample-Meteorological Relation, Surface Meteorological Data, Upper Air Meteorological Data, and Meteorological Tower Description.

These changes made the database more accurately reflect the information stored in the reports and, thus, will enhance its usefulness in the future.

6.3.5 Unique Identifiers

This approach was initiated in FY 1995 (see Section 6.2.3). Additional unique identifiers were assigned as needed in FY 1996.

6.3.6 Chemical Categorization

This approach was initiated in FY 1995. New chemicals added in FY 1996 were categorized accordingly.

6.3.7 Staff Training

One staff member attended a hands-on Sybase System 10 class in Washington D.C. for training on Sybase Systems and Transact-SQL.

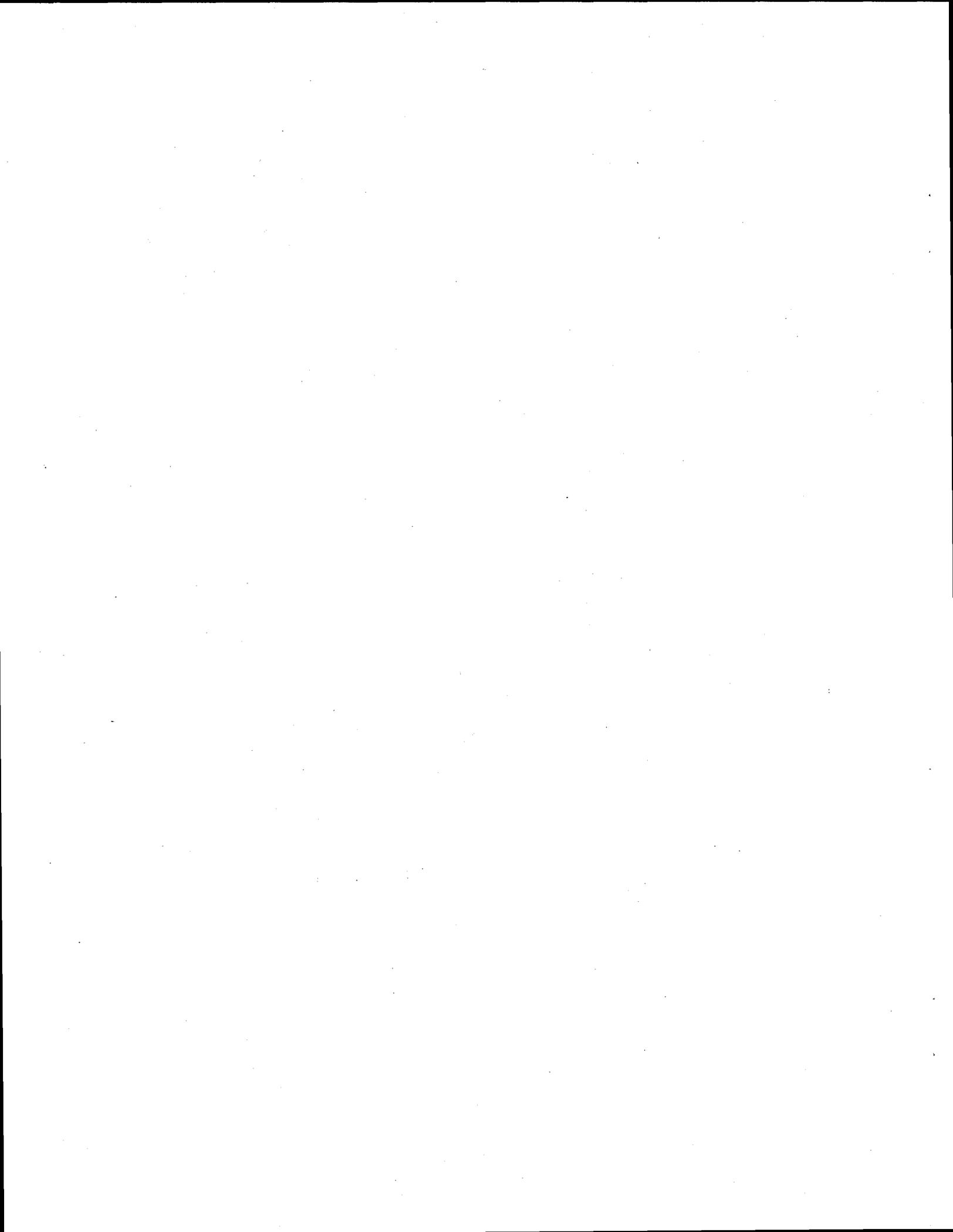
6.3.8 Review for QC Impact Level II

Review of the data and procedures was begun in FY 1996 and included review of data from thirty-seven tanks, review of the Excel Visual Basic codes used, and review of the unique identifiers and chemical categorization schemes.

6.4 Future Plans

Plans for the coming fiscal year include the following:

- Providing sample and analysis averages of data by tank
- Continuing to work with the TWINS2 staff to enhance the interface
- Loading new tank vapor data, monitoring data, and flammability data
- Fully implementing the unit conversion capabilities.



7.0 Lessons Learned

7.1 PNNL SUMMA™ and TST Analytical Laboratories

7.1.1 Need to Eliminate Coldspots in Commercially Available Vapor Analysis Systems

The design of commercially available cryoconcentrators, canister-cleaning stations, and dynamic diluters assumes that all of the compounds in the vapor sample will be volatile and water insoluble. However, tank headspace vapor samples frequently contain semivolatile and polar organic compounds. Due to the presence of these semivolatile components in tank headspace vapors [normal paraffinic hydrocarbons (NPH), alcohols, and tributyl phosphate (TBP)], elimination of coldspots in the sample acquisition, handling, and analytical equipment is essential. The heating of transfer lines, traps, and valves in currently available equipment is inadequate to prevent condensation of higher boiling point compounds on the cooler surfaces. This condensation causes two problems with the analytical system: 1) loss of compounds with the resulting poor quantitation, and 2) physical plugging or chemical trapping of other compounds over time, with the resulting deterioration of system performance. Condensation of higher boiling point compounds on SUMMA™ canister walls also increased the difficulty of cleaning the canisters.

Corrective Actions Implemented:

1. Heat tape was applied to various exposed portions of the system plumbing.
2. Heating mantles were ordered for the canisters for use with the canister-cleaning station. These were later determined to be not useful.
3. Some canisters from high organic tanks have to be cycled through the cleaning process up to three times.

7.1.2 Limited Utility of the EPA TO-14 Method

The EPA compendium method TO-14 was designed for measurements of volatile organic compounds in ambient air. Thus, the 40 compounds listed in the method are those expected in ambient samples from both urban and rural locations. They include low molecular weight chlorofluorocarbons, aromatics, aldehydes, ketones, and aliphatics. These compounds derive from refrigerants, fuel use, coatings, packaging, and chemical manufacturing. They are at least moderately stable at ambient temperatures and pressures and in the presence of ultraviolet light. This list of 40 compounds has turned out to be of limited use for the analysis of tank headspace vapor samples. Some tanks have had as few as two TO-14 compounds in their vapor samples. These differences reflect the environment in the tanks, which includes higher than ambient temperatures (40°C), high molecular weight starting materials (NPH, TBP), and the presence of radiolytic decomposition products. Compound classes included higher molecular weight aliphatic compounds, alcohols, nitriles, ketones, aldehydes, and alkenes.

Corrective Actions Implemented: The TO-14 Method was modified to accommodate the differences in analytes. The modifications included changes in sample handling, analytical conditions, and standards.

1. As mentioned above, heat was applied at various stages of the sample handling to prevent condensation on cold spots.
2. The Nafion™ dryer was eliminated from the cryoconcentration step because of its effect on polar compounds.
3. The gas chromatography column, temperature program and run times were altered to accommodate higher boiling point compounds.
4. A heated loop injector was constructed for more concentrated samples.
5. The holding time of SUMMA™ canisters prior to analysis had not previously been determined for tank headspace samples. Data that are currently available on holding times relate to ambient air type samples. A holding time study was implemented at the end of FY 1996 and will continue into FY 1997.

7.1.3 Quality Assurance/Quality Control

QA/QC for Hanford tank headspace samples is complicated by the fact that the EPA TO-14 procedure as written is not directly applicable to the tank headspace vapor samples.

Corrective Actions Implemented:

1. Gas standards containing compounds more relevant to tank atmospheres were created using a permeation tube system. Running of the TO-14 standards was continued because of their traceability and as a check of the systems performance. To minimize the number of standards run, the tank standards and TO-14 standards were usually mixed prior to analysis.
2. A total of six procedures were written and approved for the analysis of tank headspace vapor samples.

7.1.4 Contamination of TST's in ISVS System

A number of analytes have been found in TST field blanks from ISVS sampling jobs. Compounds identified include alkanes, cycloalkanes, alcohols and a chlorofluorocarbon. It was thought that the hydrocarbons and alcohols might originate from the tape being used to hold together the sampler. However, subsequent investigations have failed to indicate that all of the contamination is coming from the tape. The source of the chlorofluorocarbon has not yet been determined. These contaminants are also seen in tank samples from these jobs.

Corrective Actions Implemented: Analyses have been performed of the various materials used in the ISVS sampling (tape, gloves, etc.) A "bundle study" of the assembled ISVS sample bundle was also conducted. Only some of the contaminants have been identified in this manner. The search is continuing. A new location for preparing the sample bundles has also been identified.

7.1.5 Large Range of Analyte Concentration in Tank Headspace Vapor Samples

Initial TO-14 analyses of S-102 and BY-108 showed that certain constituents, particularly N-butanol were present in the samples at concentrations higher than the calibration studies. Our TO-14 procedure requires that in these circumstances, the samples be diluted and rerun until all analytes can be analyzed at concentrations below the highest calibrations standard.

Corrective Actions Implemented: The S-102 samples had to be diluted and rerun once. The BY-108 samples required two dilutions and reruns to achieve this objective.

7.1.6 Difficulty of Water Management in Tank Headspace Vapor Samples

The EnTek 7000 cryoconcentrator for both TO-14 Systems 1 and 2 began to malfunction, resulting in an inability to achieve calibration objectives for the TO-14 method. The problem has been traced to water management in the system using the micro-scale purge and trap method. The problem was ultimately corrected, but resulted in a 10-week downtime for the TO-14 method.

Corrective Actions Implemented: The EnTek 7000 for TO-14 System 1 was rebuilt in the laboratory. The EnTek 7000 for TO-14 system 2 was returned to the factory for reconditioning. After its return, an EnTek factory representative visited the vapor laboratory on July 1 and 2. As a result, the problems with both EnTek 7000 cryoconcentrator systems were solved. The project now has two operational TO-14 systems. Additionally, the TO-12 EnTech 7000 cryoconcentrator for System 3 was rebuilt after a cryo-solenoid malfunction. This was also part of the set-up and troubleshooting after the system move from 326/23-B to 329/126.

7.1.7 Wide Range of Physical and Chemical Properties of Tank Headspace Analytes

Analytes in the tank vapor headspace samples exhibit a wide range of both physical and chemical properties. Compounds range from volatile to semivolatile and from polar to non-polar. Most chemical analysis methods are focused on a much narrower range of properties. Because of problems the EnTek systems had coping with this wide variety of properties, an alternate type of cryoconcentrator, manufactured by NuTek, was tried.

Corrective Actions Implemented: A NuTek system, which had been purchased by the project in FY 1995, was set up in the laboratory. A service representative from NuTek visited our laboratory and assisted with the set up. Unfortunately, tests with the NuTek cryoconcentrator indicated that this device will not be suitable for tank headspace samples since it handles polar compounds even less adequately than the EnTek systems and exhibited serious water management problems with the tank headspace samples. Therefore, it is necessary to keep the EnTek concentrators fully functional.

7.1.8 Data Handling and Reporting

Data handling and subsequent report preparation is a very labor-intensive process. Data from the laboratory are received in comma separated value (CSV) files. The CSV files correspond to the TO-14 or TST analysis of a specific sample collected from the tank headspace. A single CSV file contains the analytical results for 66 target analytes and a variable number of tentatively identified compounds (TICs). Tentatively identified compounds have ranged from 0 to as many as 100. Manual data extraction has been used to create the summary tables in the reports. Manual methods have a potential for transcription error and are very time consuming.

Corrective Actions Implemented: A data extraction routine has been developed to extract data from the CSV files and generate the report tables. This data extraction routine has been 100% verified and has been used to generate reports tables starting in September 1996.

7.1.9 Report Tables

With the addition of TST analyses, the report tables were shortened to display only detected analytes rather than all the analytes. Because the database includes analytes that are below detection, the database data reviewer found it very difficult to verify the entries against the reports.

Corrective Action Implemented: The reports for 1997 analyses will contain a full table of analytes in the appendix. For other reports, the reviewer will be provided with the procedure document that is listed in the report.

7.2 PNNL Inorganic Laboratories

7.2.1 Need to Prepare and Use Matrix-Matched Standards for the analyses of NH₃ and NO_x Sorbent Tube Leachates

Standards used in the analytical procedure for determining NH₃ should be preserved with 50μL conc. H₂SO₄/100mL standard. Standards prepared in this way effectively matrix-match DIW leachates of H₂SO₄-impregnated carbon bead sorbent tubes. Even low level standards (~1 ppm NH₃) preserved in this manner are stable for up to two weeks, although typically, working standards are prepared from stock solution on the day of actual analysis.

Standards used in the analytical procedure for determining NO₂-derived from NO_x sorbent tube trains should be prepared in desorbing solution matrix (1.5% triethanolamine in DIW). Equivalent concentrations of nitrite in DIW and desorbing matrix solution can yield significantly different chromatographic responses. Ion chromatograms of matrix matched standards and sorbent tube leachates are surprisingly complex. The analyst needs to be sure the correct peak in the chromatogram is identified with the target analyte, NO₂⁻.

7.2.2 Need to Modify Standard Anion Ion-Chromatography Conditions for Analysis of Nitrite

Standard suppressed conductivity ion chromatographic conditions routinely used for common anions in simple aqueous matrices are not adequate to resolve the analyte peak (NO₂⁻) from interfering matrix peaks. Non-standard eluent and chromatographic column configuration have been employed to adequately resolve the target analyte from matrix interference peaks (see section A.2.2 of any recent PNNL Headspace Vapor Characterization report).

7.2.3 Observation

In only a few tanks have NO₂ and NO been found in concentrations above EQL. In fact, of all the tanks sampled so far, neither NO₂ nor NO have been found to be present at concentrations within 10% of notification levels (10 ppmv and 50 ppmv for NO₂ and NO, respectively).

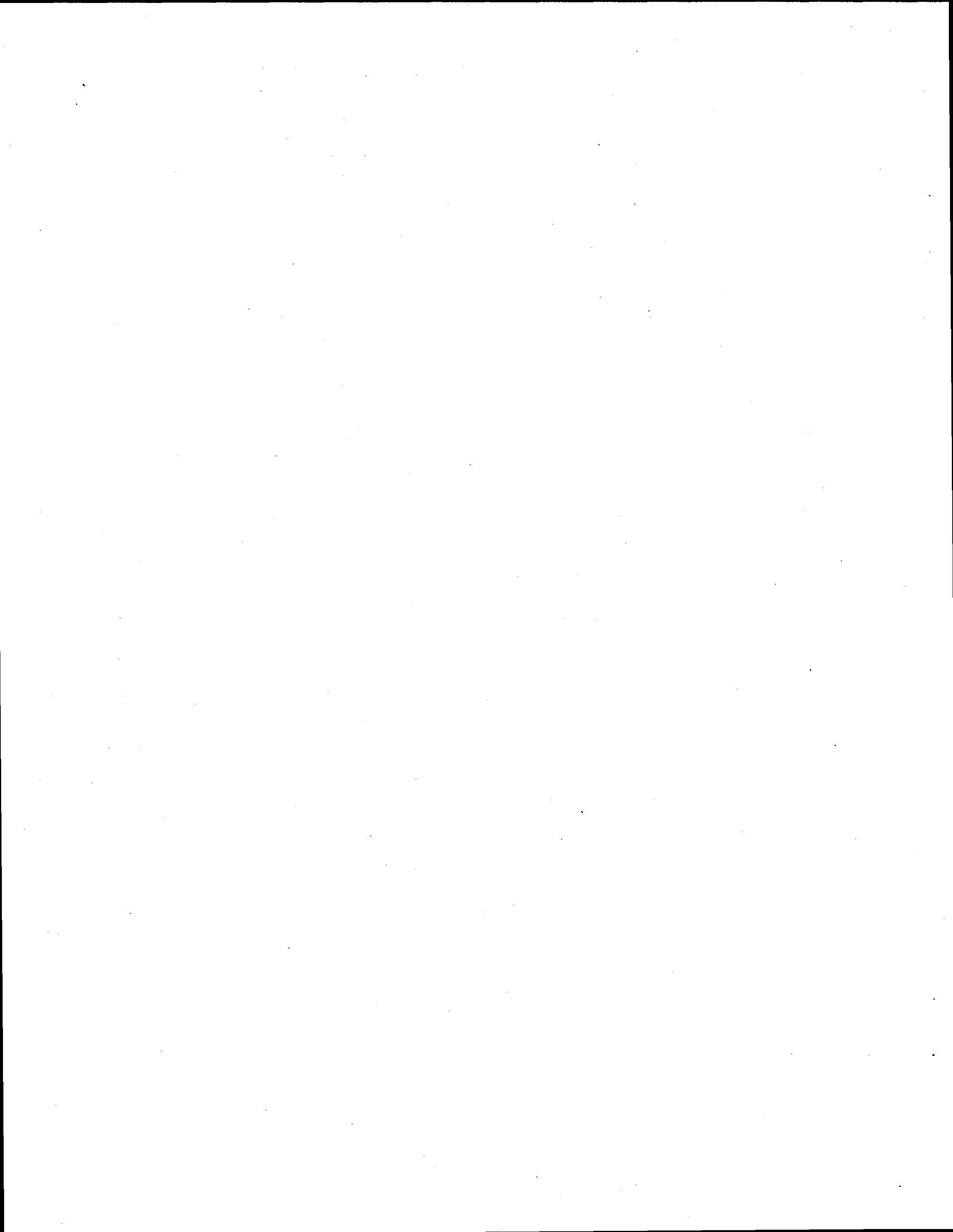
7.3 Quality Assurance

7.3.1 Implementation of HASQAP Requirements

HASQAP requirements were incorporated into the Project's Quality Assurance Plan ETD-002 and implemented. During the year, it was necessary to deviate from the prescribed requirements in the QA Plan due to changes in instrument performance, special SAP requirements, and various implementation issues. Additionally, both internal and external assessments were performed, which noted that necessary clarifications/additions were required in the QA Plan and/or procedures.

Corrective Actions Implemented:

1. Deviation Reports were issued according to the QA Plan, which documented the changes and their justification.
2. Several analytical procedures and the QA Plan were revised to incorporate permanent changes as a result of Deviation Reports and assessment corrective actions.

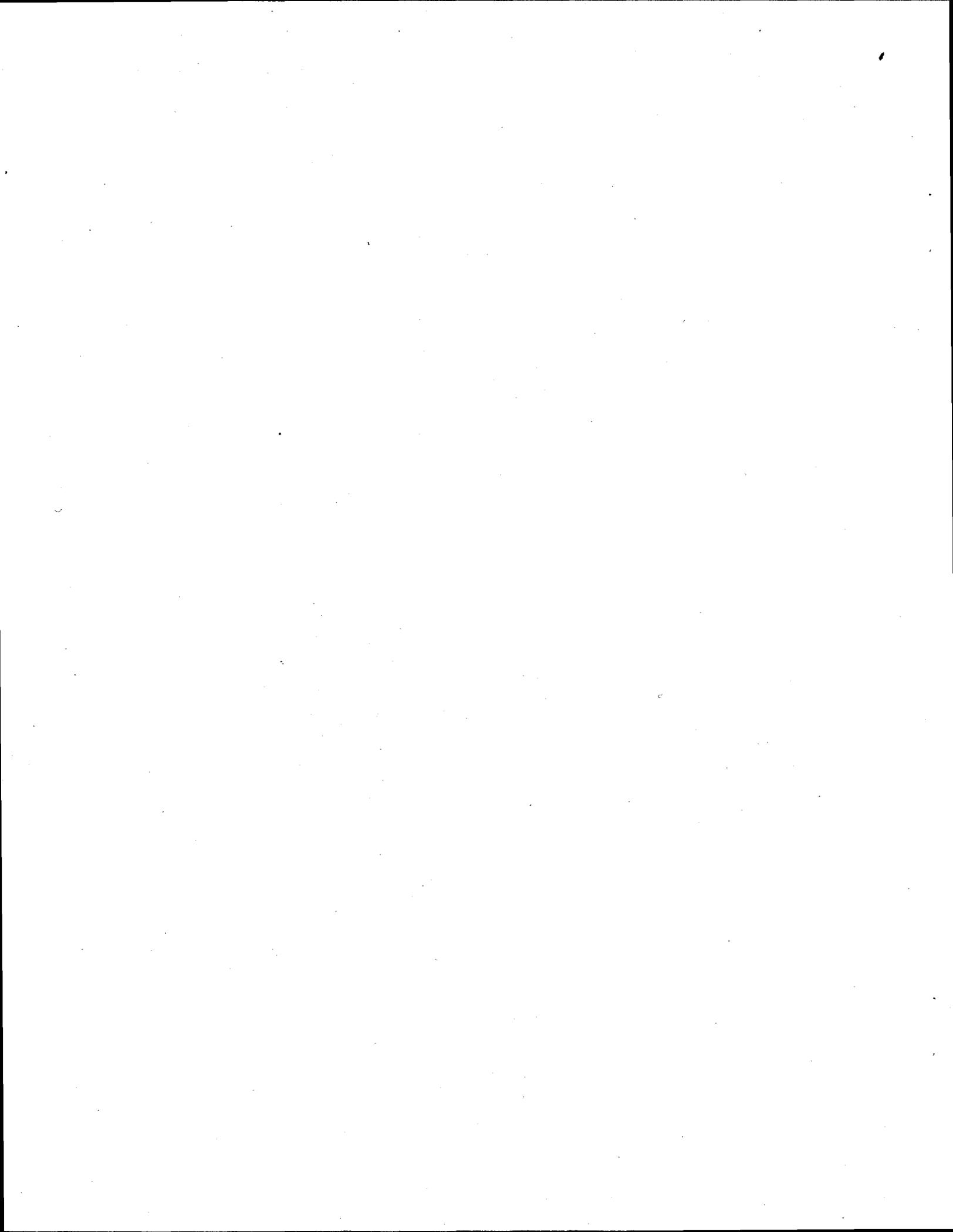


8.0 References

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

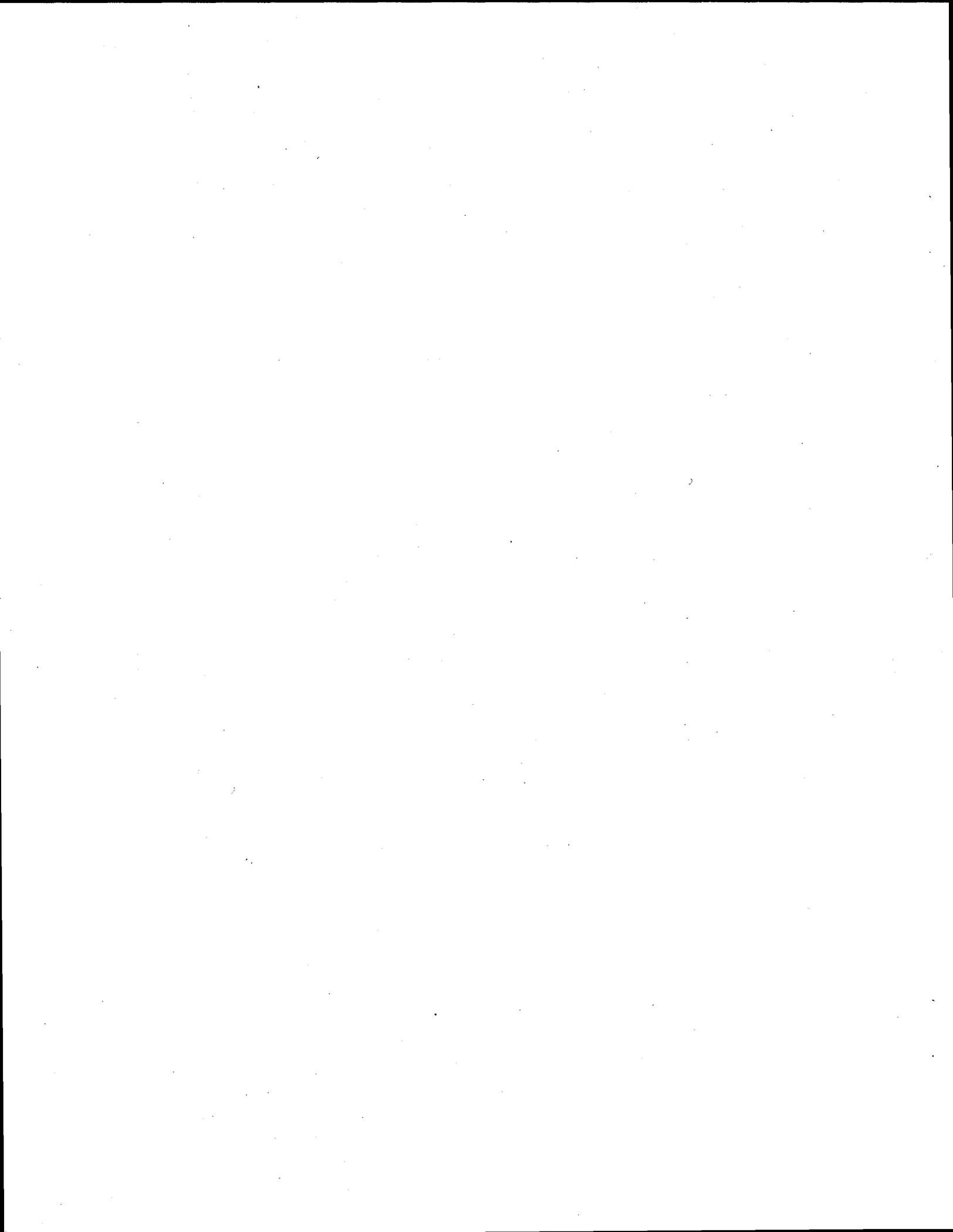
Ligothke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94 - 5/25/94)*. PNL-10172, Pacific Northwest National Laboratory, Richland, Washington.

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



Appendix A

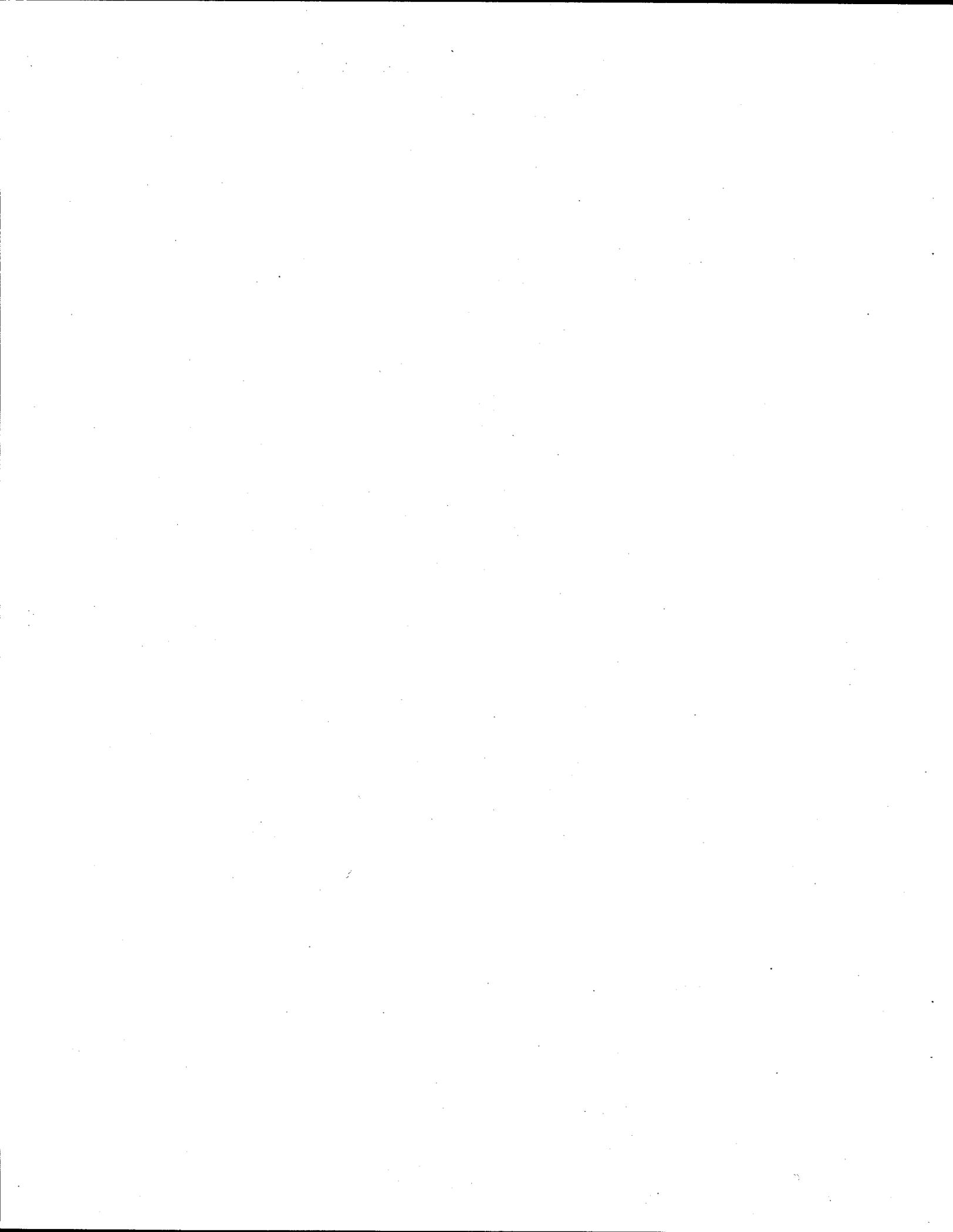
List of Current Technical Procedures for the PNNL Tank Vapor Characterization Project



Appendix A

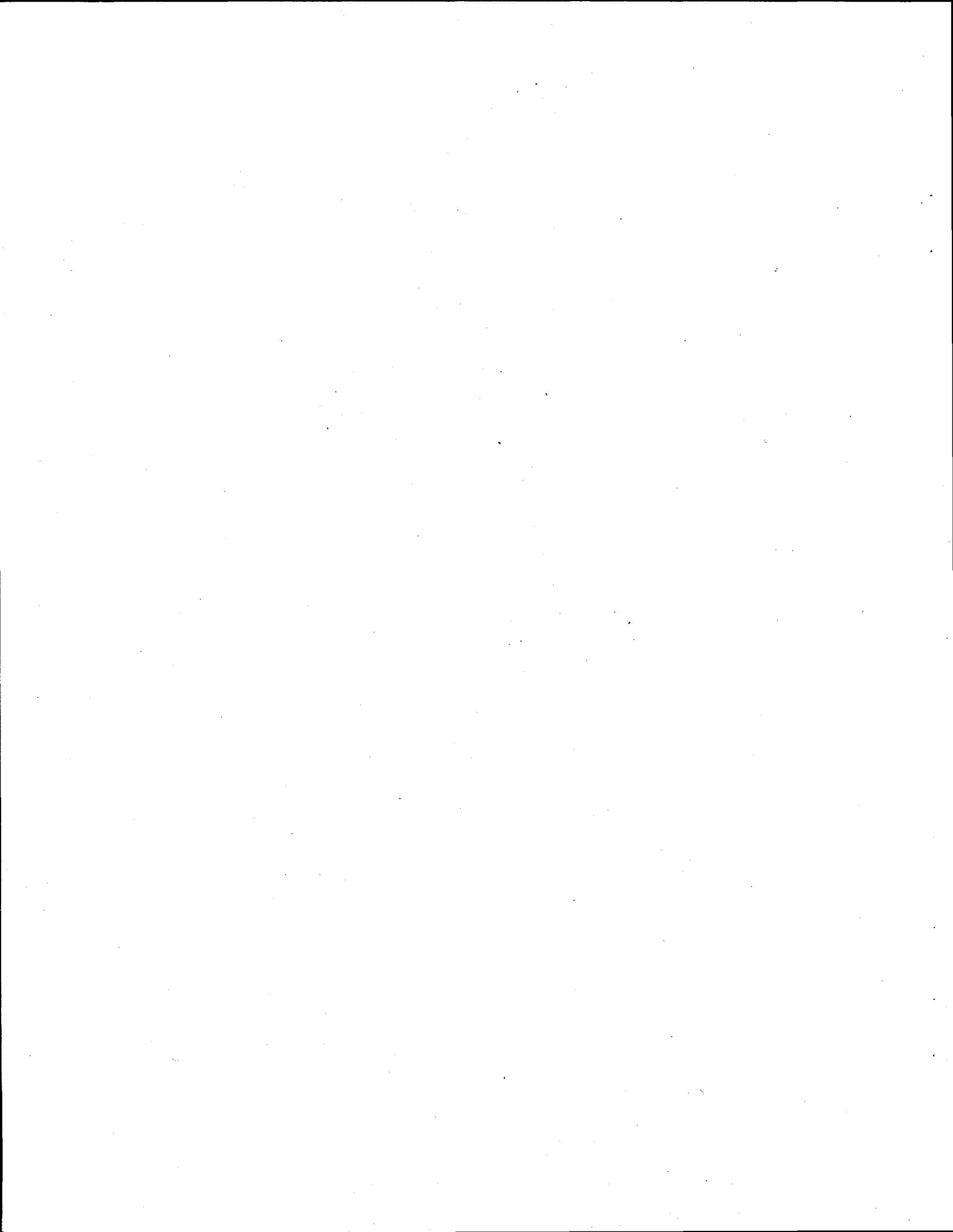
List of Current Technical Procedures for the PNNL Tank Vapor Characterization Project

Procedure	Date	Title
PNL-TVP-02, Rev. 0	August 1994	Cleaning SUMMA™ canisters and the validation of the cleaning process.
PNL-TVP-03, Rev. 2	August 1996	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. 2	May 1996	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. 2	December 1995	Shipping, receiving, and handling procedure for PNL waste tank samples.
PNL-TVP-08, Rev. 1	December 1995	Determination of TO-12 total non-methane organic compounds in Hanford waste tank headspace using SUMMA™-passivated canister sampling and flame ionization detection.
PNL-TVP-09, Rev. 2	December 1995	Sorbent trap preparation for sampling and analysis: waste tank inorganic vapor samples.
PNL-TVP-10, Rev. 2	February 1996	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

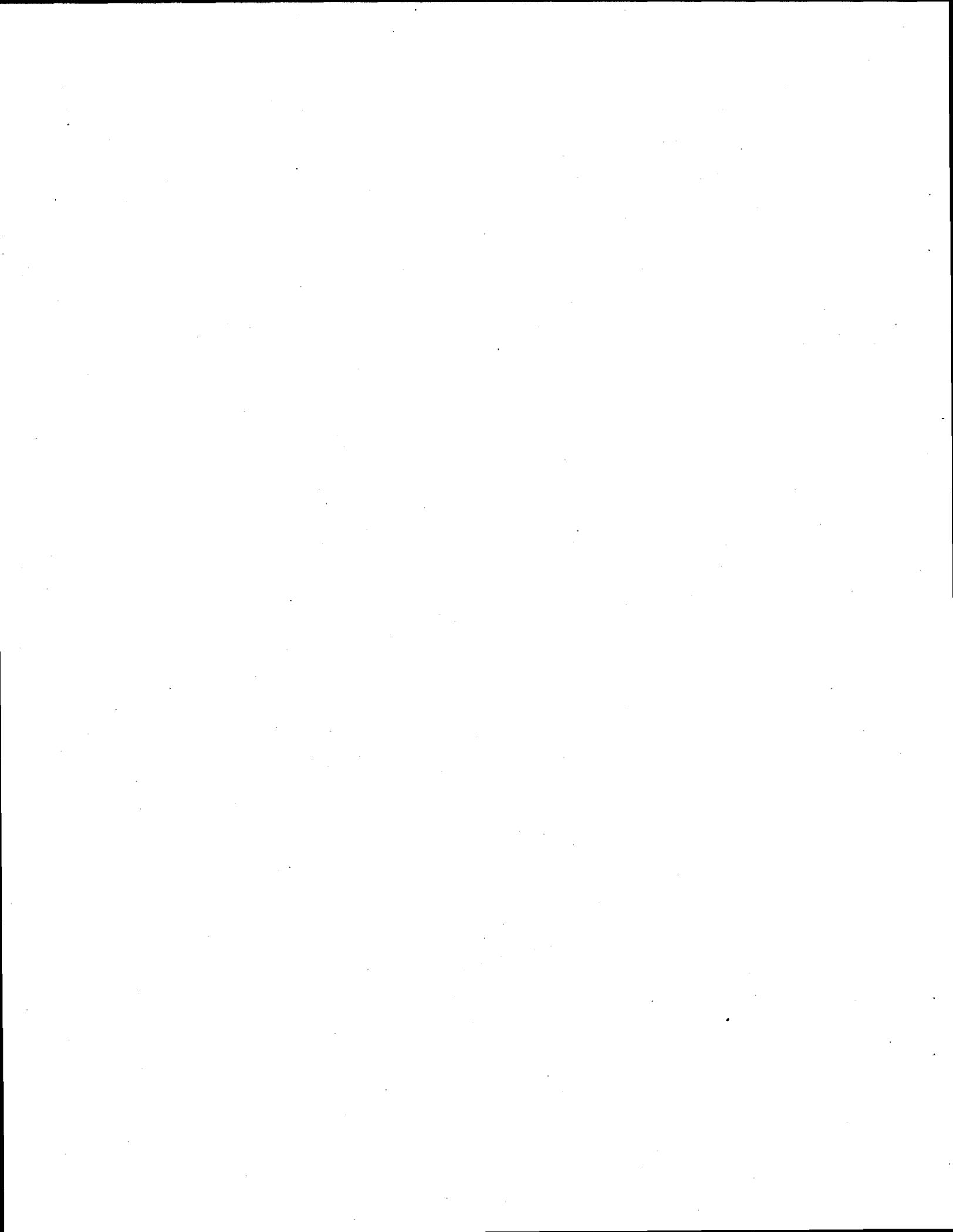
Tank Vapor Characterization Data Reports -- FY 1996



Appendix B

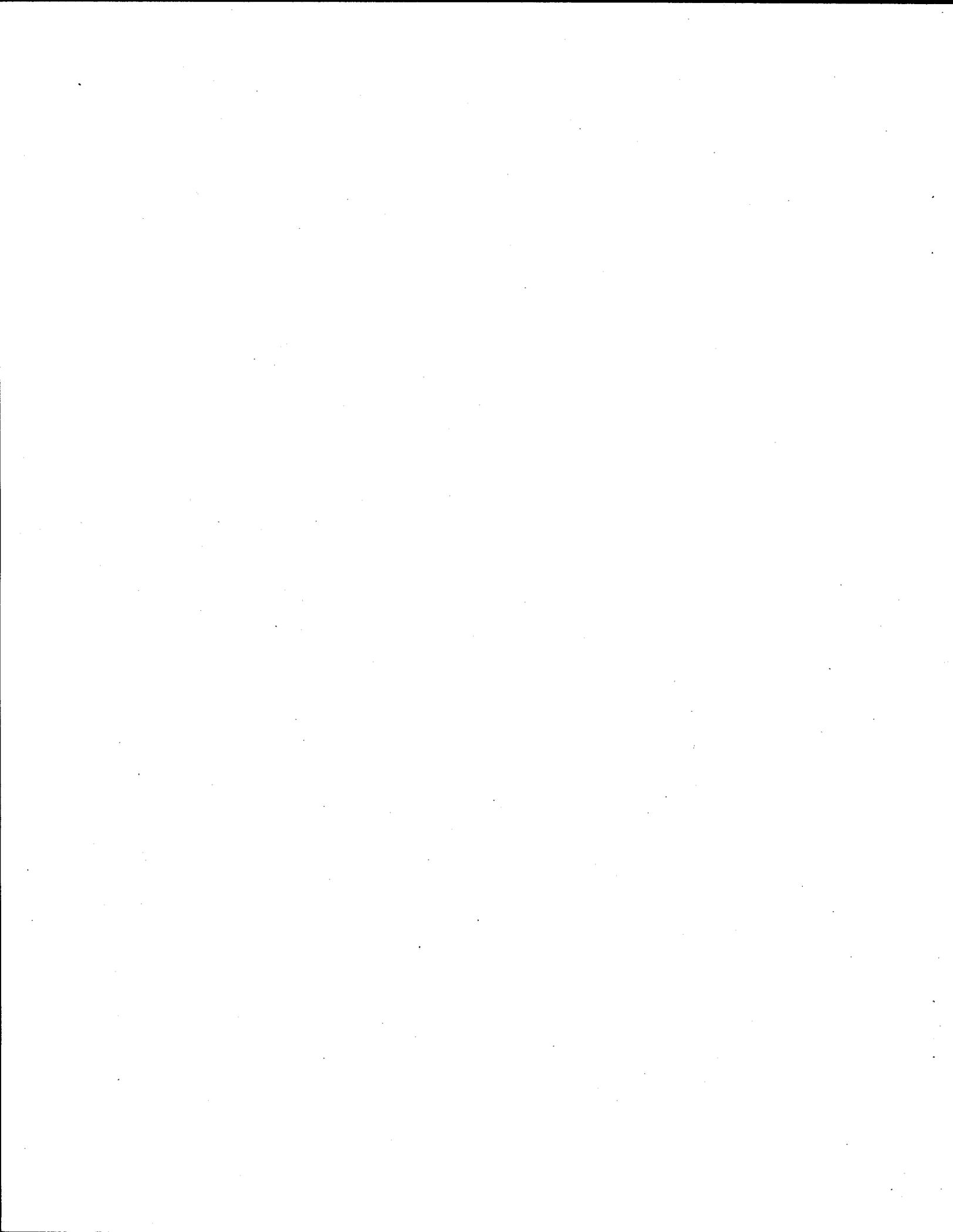
Tank Vapor Characterization Data Reports -- FY 1996

Tank	Sample Job Number	Tank Sample Date	Draft Report	Final Report
FY95 Sample Jobs, Reports Completed in FY 1996:				
AX-101	S5028	6/15/95	10/95	5/22/96
AX-103	S5029	6/21/95	10/95	5/22/96
SX-101	S5045	7/21/95	10/19/95	5/22/96
SX-102	S5046	7/19/95	10/19/95	5/22/96
SX-104	S5049	7/25/95	11/95	5/22/96
SX-105	S5047	7/26/95	12/29/95	5/22/96
SX-109	S5048	8/1/95	12/29/95	5/22/96
U-108	S5054	8/29/95	2/2/96	5/22/96
S-112	S5044	7/11/95	9/27/95	5/30/96
T-110	S5056	8/31/95	1/30/96	5/30/96
U-109	S5055	8/10/95	1/26/96	5/30/96
FY96 Sample Jobs, Reports Completed in FY 1996:				
TX-111	S5069	10/12/95	11/27/95	6/25/96
A-103	S5073	11/9/95	4/24/96	6/12/96
A-102	S5074	11/10/95	3/25/96	6/5/96
BX-107	S5080	11/17/95	3/19/96	6/6/96
BY-102	S5081	11/21/95	4/26/96	6/12/96
S-105	S5084	12/5/95	3/19/96	6/17/96
S-110	S5085	12/6/95	3/19/96	6/20/96
S-108	S5086	12/7/95	3/19/96	6/17/96
C-107a	S6001	1/17/96	4/3/96	7/10/96
C-107b	S6002	1/17/96	4/3/96	7/10/96
C-107c	S6003	1/17/96	4/3/96	7/10/96
BY-108a	S6004	1/23/96	4/19/96	7/25/96
BY-108b	S6005	1/23/96	4/19/96	7/25/96
BY-108c	S6006	1/23/96	4/19/96	7/25/96
S-102a	S6007	1/26/96	4/18/96	7/23/96
S-102b	S6008	1/26/96	4/18/96	7/23/96
S-102c	S6009	1/26/96	4/18/96	7/23/96
T-104	S6012	2/7/96	4/26/96	6/13/96
C-107 d	S6019	3/26/96	8/30/96	11/25/96
C-107 e	S6020	3/26/96	8/30/96	11/25/96
S-102 d	S6030	4/4/96	9/18/96	11/20/96
S-102 e	S6031	4/4/96	9/18/96	11/20/96
BY-108 d	S6021	3/28/96	9/30/96	11/20/96
BY-108 e	S6022	3/28/96	9/30/96	11/20/96
TY-102	S6037	4/12/96	9/12/96	10/25/96
B-102	S6044	4/18/96	7/30/96	8/16/96
BX-105	S6045	4/24/96	8/7/96	10/18/96
BX-110	S6046	4/30/96	9/10/96	10/25/96
S-109	S6057	6/4/96	8/14/96	10/18/96
S-101	S6058	6/6/96	9/24/96	11/11/96
S-103	S6060	6/12/96	9/19/96	10/31/96
S-106	S6061	6/13/96	9/20/96	11/12/96
S-107	S6062	6/18/96	9/5/96	10/19/96
C-201	S6065	6/19/96	8/30/96	10/19/96
C-202	S6066	6/25/96	9/18/96	10/24/96
C-204	S6067	7/2/96	9/27/96	11/12/96
U-112	S6071	7/9/96	9/23/96	11/12/96
B-202	S6073	7/18/96	9/5/96	10/24/96
B-107	S6074	7/23/96	9/26/96	11/13/96
B-105	S6075	7/30/96	9/27/96	11/12/96
FY96 Sample Jobs, Reports to be Completed in FY 1997:				
U-104	S6072	7/16/96		
BX-102	S6080	7/31/96		
BX-103	S6081	8/1/96		
BX-106	S6082	8/15/96		
BX-111	S6083	8/20/96		
BY-101	S6084	8/29/96		
BX-104	S6086	8/22/96		
C-107	S6091	9/5/96		
BY-108	S6092	9/10/96		
S-102	S6093	9/19/96		



Appendix C

Tank Vapor Database Information



Appendix C

Tank Vapor Database Information

241-A-101	241-S-102
241-A-102	241-S-105
241-A-103	241-S-108
241-AX-101	241-S-110
241-AX-102	241-S-111
241-AX-103	241-S-112
241-B-102	241-SX-101
241-B-103	241-SX-102
241-BX-104	241-SX-103
241-BX-107	241-SX-104
241-BY-102	241-SX-105
241-BY-103	241-SX-106
241-BY-104	241-SX-109
241-BY-105	241-T-104
241-BY-106	241-T-107
241-BY-107	241-T-110
241-BY-108	241-T-111
241-BY-110	241-TX-105
241-BY-111	241-TX-111
241-BY-112	241-TX-118
241-C-101	241-TY-101
241-C-102	241-TY-103
241-C-103	241-TY-104
241-C-104	241-U-103
241-C-105	241-U-105
241-C-106	241-U-106
241-C-107	241-U-107
241-C-108	241-U-108
241-C-109	241-U-109
241-C-110	241-U-111
241-C-111	241-U-203
241-C-112	241-U-204



Appendix D

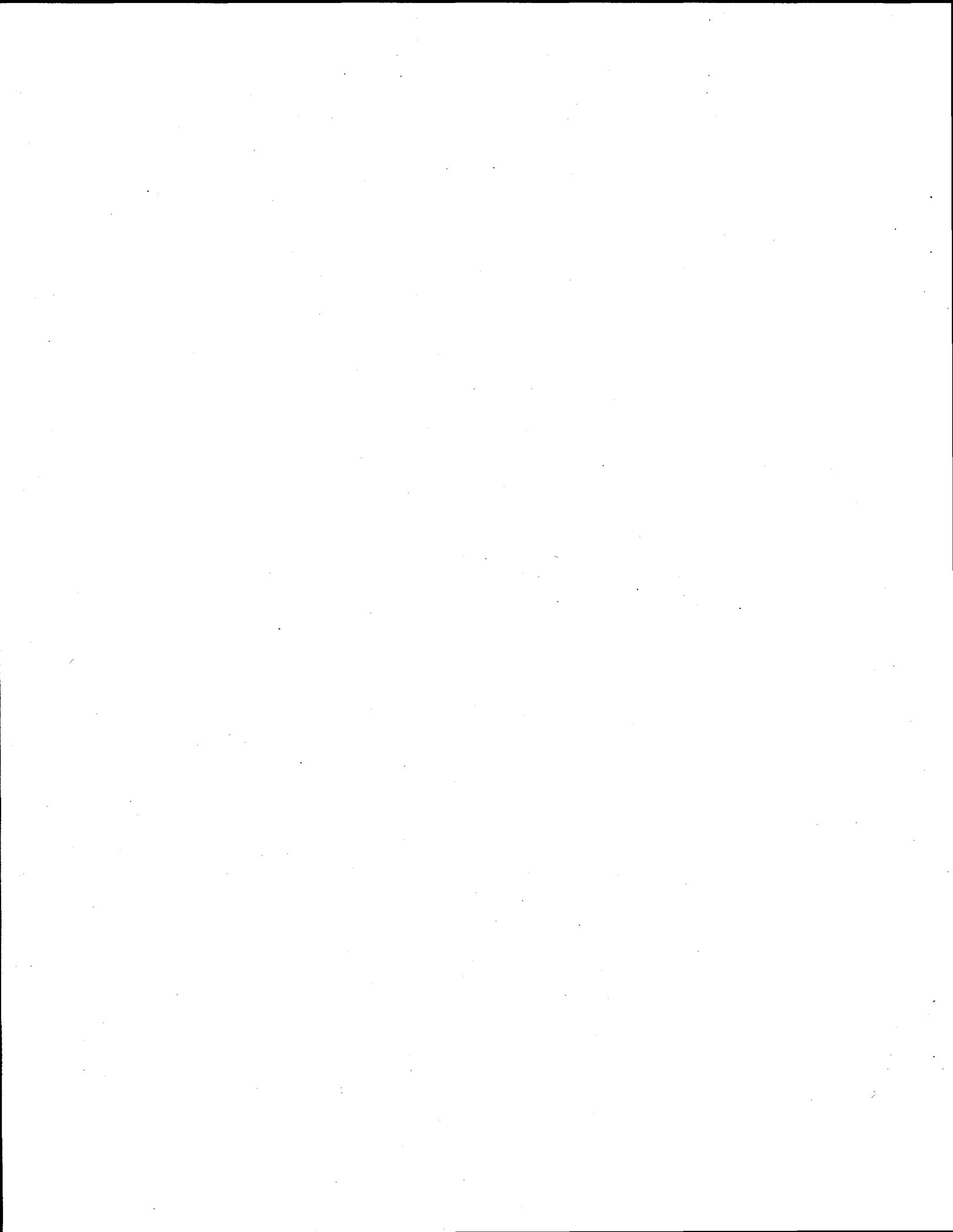
Tanks with FY 1996 Monitoring Data Contained in Database



Appendix D

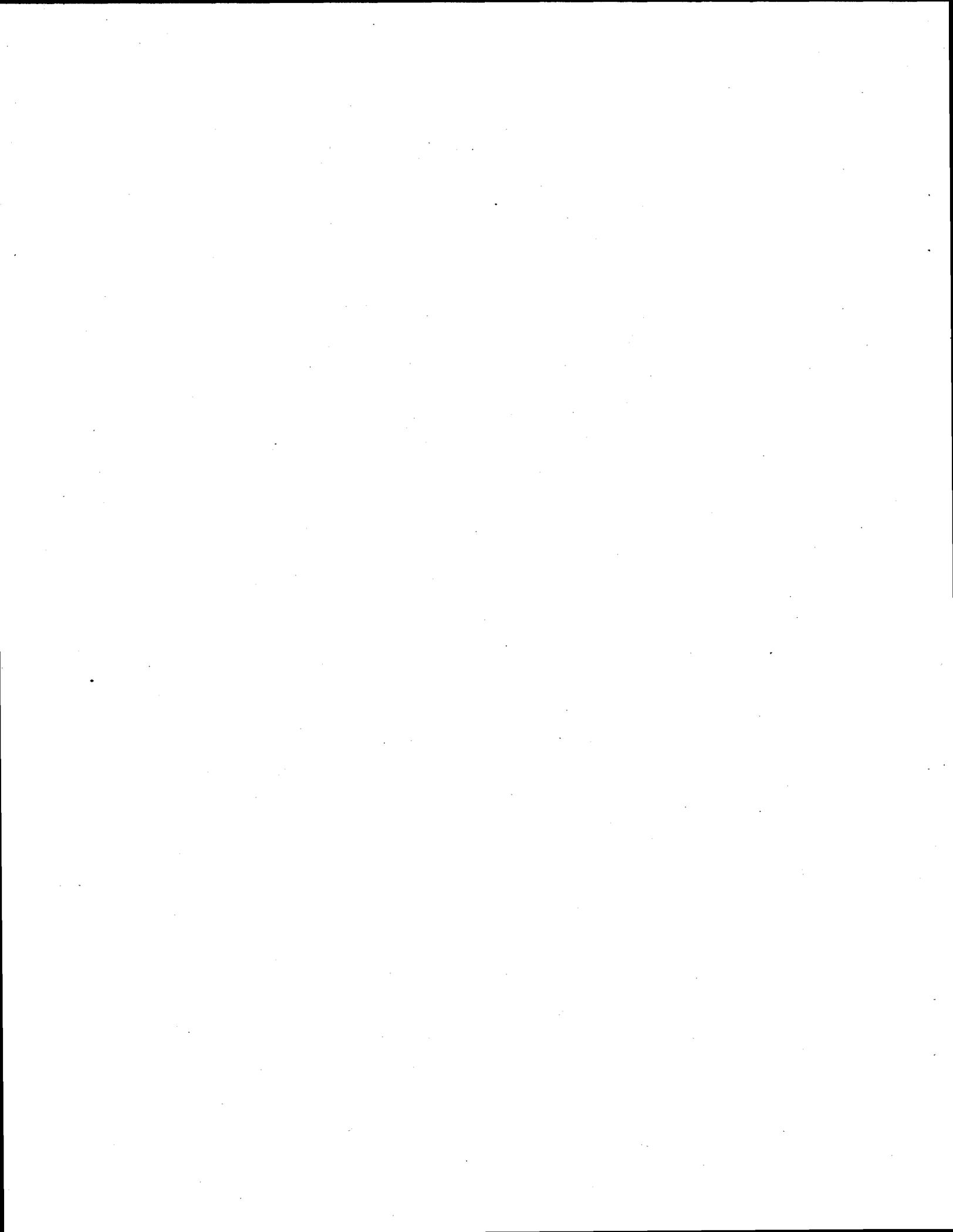
Tanks with FY 1996 Monitoring Data Contained in Database

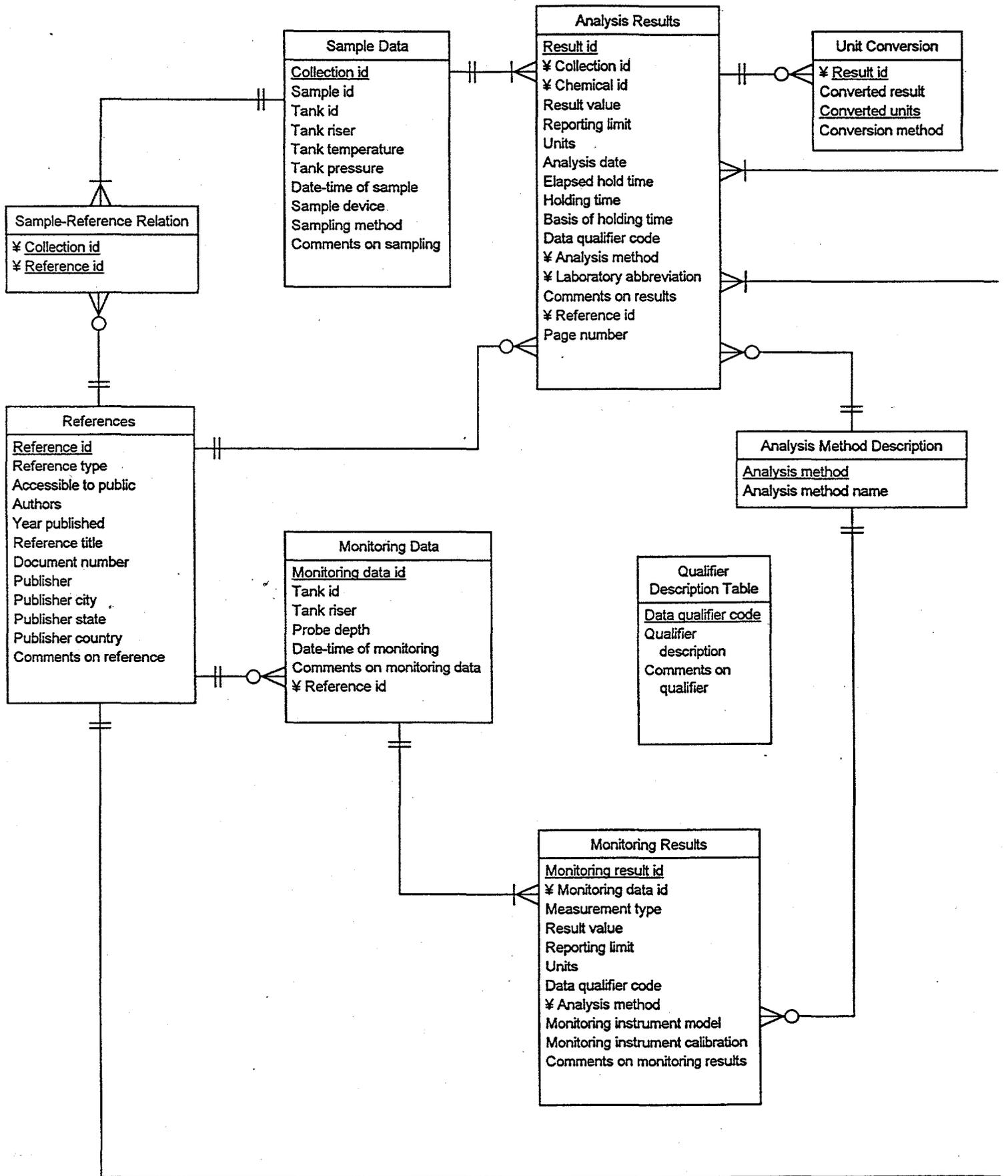
241-A-104	241-T-101
241-A-105	241-T-102
241-A-106	241-T-103
241-B-101	241-T-105
241-B-104	241-T-106
241-B-105	241-T-108
241-B-106	241-T-109
241-B-107	241-T-112
241-B-108	241-T-201
241-B-109	241-T-202
241-B-110	241-T-204
241-B-111	241-TX-101
241-B-201	241-TX-102
241-B-202	241-TX-103
241-B-204	241-TX-104
241-BX-101	241-TX-106
241-BX-103	241-TX-108
241-BX-106	241-TX-109
241-BX-109	241-TX-110
241-BX-110	241-TX-112
241-BX-111	241-TX-113
241-BY-101	241-TX-114
241-BY-109	241-TX-115
241-C-204	241-TX-116
241-S-101	241-TX-117
241-S-103	241-TY-105
241-S-104	241-U-101
241-S-106	241-U-102
241-S-109	241-U-104
241-SX-115	241-U-112

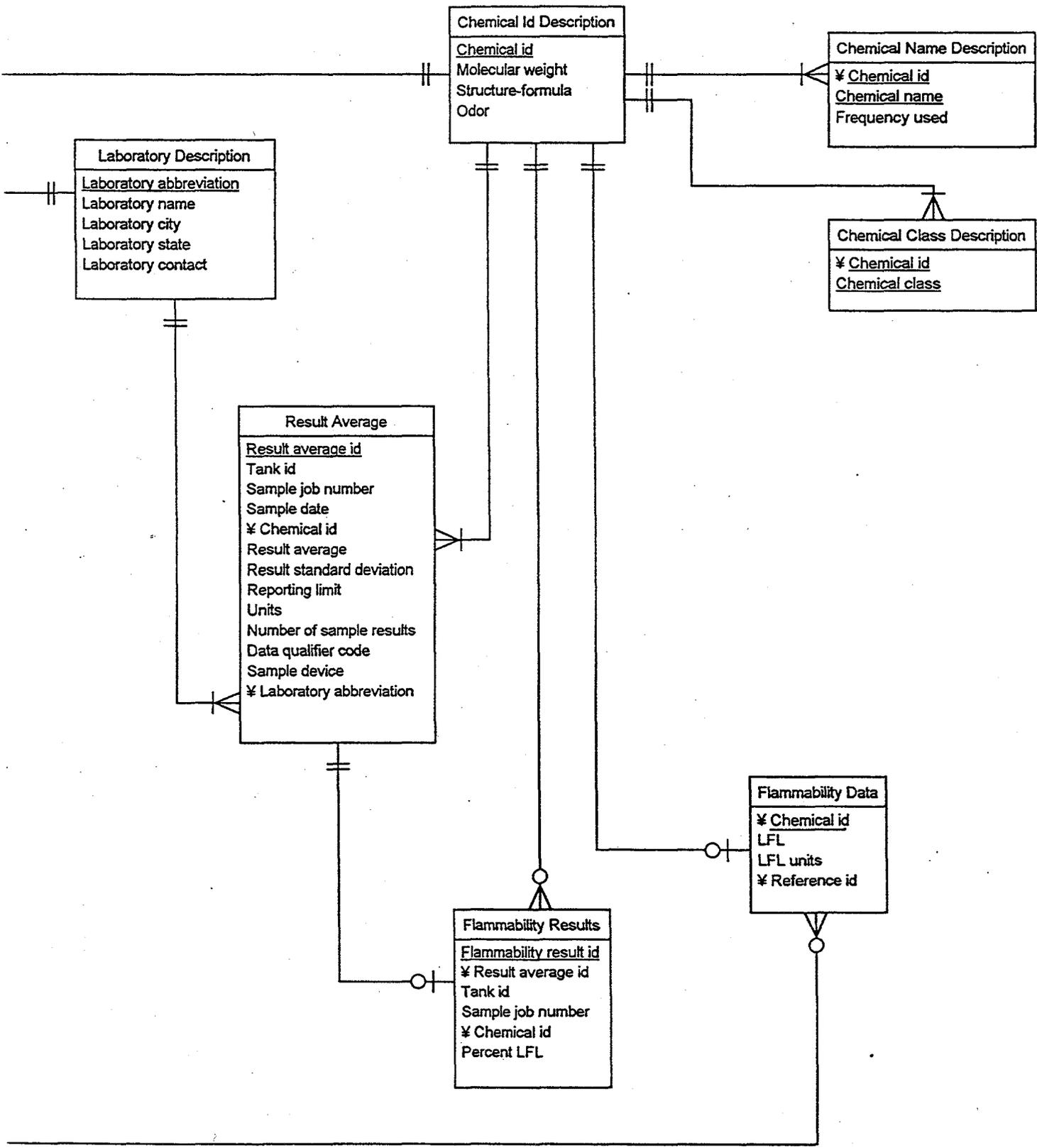


Appendix E

Data Model







Appendix F

Data Dictionary

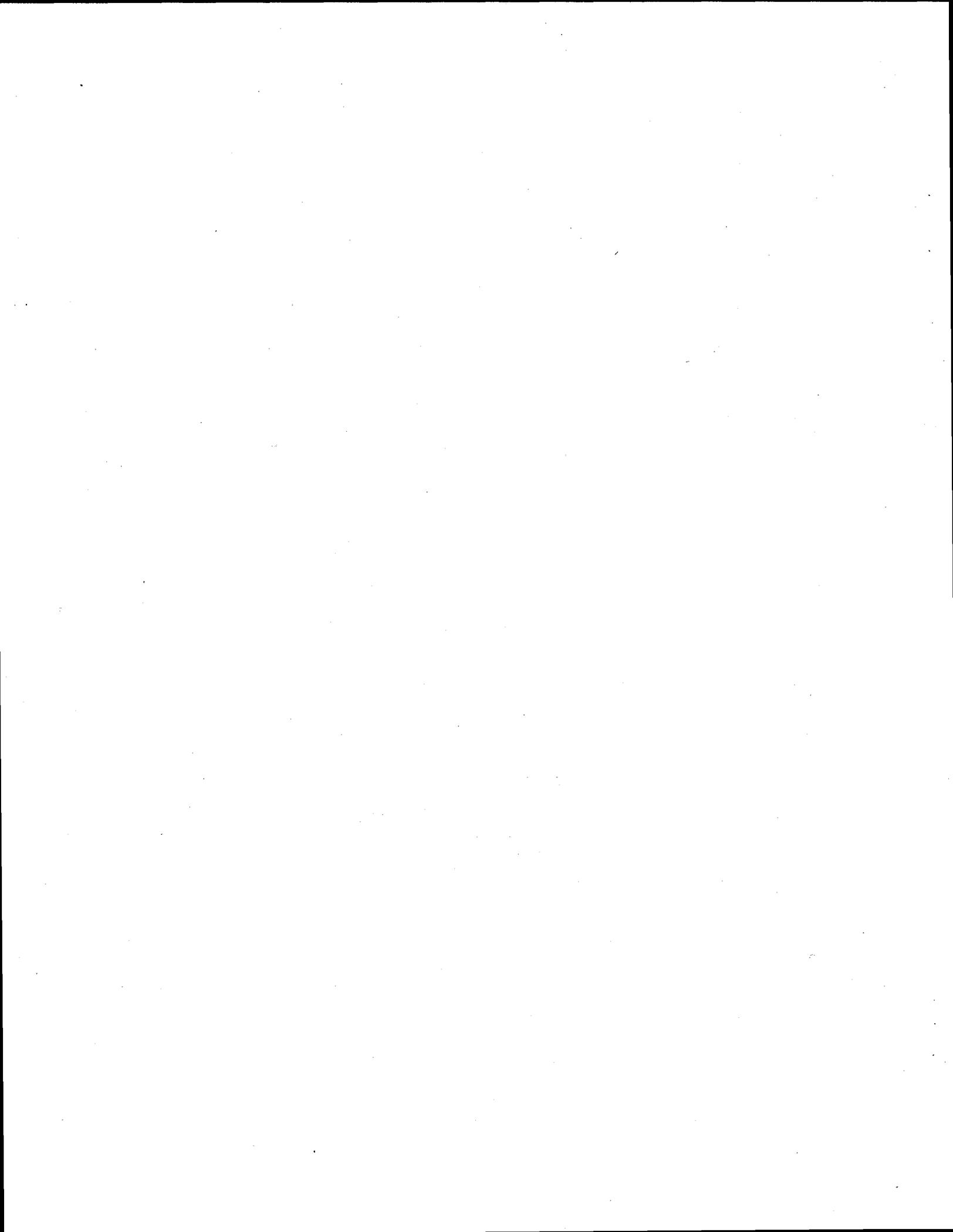


Table Descriptions

Table Name	Description
------------	-------------

Analysis Method Description	This table provides information about the method used to analyze the sample.
-----------------------------	--

Entity Name	Key Field?	Nulls Allowed?
Analysis method	Yes	No
Analysis method name	No	No

Analysis Results

This table contains the concentration of a specific chemical analyzed from the sample. Other information contained includes analytical method, laboratory that performed the analysis, any qualifiers on the data, and a link to the reference citation. This information is generally taken directly from published reports.

Table Name Description

Entity Name	Key Field?	Nulls Allowed?
Result id	Yes	No
Collection id	No	No
Chemical id	No	No
Result value	No	Yes
Reporting limit	No	Yes
Units	No	No
Analysis date	No	Yes
Elapsed hold time	No	Yes
Holding time	No	Yes
Basis of holding time	No	Yes
Data qualifier code	No	Yes
Analysis method	No	No
Laboratory abbreviation	No	No
Comments on results	No	Yes
Reference id	No	No
Page number	No	Yes

Chemical Class Description This table provides the primary chemical categories for each chemical constituent.

Entity Name	Key Field?	Nulls Allowed?
Chemical id	Yes	No
Chemical class	Yes	No

Chemical Id Description

This table contains the Chemical Abstract Services number, if available, or unique identifier code for every chemical of interest in the tank vapor studies. Also, this table contains the molecular weight, condensed structural-formula, and odor of the chemical.

Table Name Description

Entity Name	Key Field?	Nulls Allowed?
Chemical id	Yes	No
Molecular weight	No	Yes
Structure-formula	No	Yes
Odor	No	Yes

Chemical Name Description
 This table provides the standard names and synonyms for a chemical. It also provides a chemical id, which is the Chemical Abstract Services (CAS) number or a unique identifier code.

Entity Name	Key Field?	Nulls Allowed?
Chemical id	Yes	No
Chemical name	Yes	No
Frequency used	No	No

Flammability Data
 This table contains literature values for the lower flammability limit in air for selected analytes.

Entity Name	Key Field?	Nulls Allowed?
Chemical id	Yes	No
LFL	Yes	No
LFL units	No	No
Reference id	No	No

Flammability Results
 This table provides headspace flammability data, expressed as percent of Lower Flammability Level (LFL), for selected analytes for the specified tanks, by sample job number.

Table Name Description

Entity Name	Key Field?	Nulls Allowed?
Flammability result id	Yes	No
Result average id	No	No
Tank id	No	No
Sample job number	No	No
Chemical id	No	No
Percent LFL	No	No

Laboratory Description This table contains location information about the laboratories that performed the sample analyses.

Entity Name	Key Field?	Nulls Allowed?
Laboratory abbreviation	Yes	No
Laboratory name	No	No
Laboratory city	No	Yes
Laboratory state	No	Yes
Laboratory contact	No	Yes

Monitoring Data This table contains information about the collection of industrial hygiene field monitoring data.

Table Name Description

Entity Name	Key Field?	Nulls Allowed?
Monitoring data id	Yes	No
Tank id	No	No
Tank riser	No	No
Probe depth	No	No
Date-time of monitoring	No	No
Comments on monitoring data	No	Yes
Reference id	No	No

Monitoring Results
 This table contains industrial hygiene field monitoring results for in-tank measurements.

Entity Name	Key Field?	Nulls Allowed?
Monitoring result id	Yes	No
Monitoring data id	No	No
Measurement type	No	No
Result value	No	Yes
Reporting limit	No	Yes
Units	No	No
Data qualifier code	No	Yes
Analysis method	No	No
Monitoring instrument model	No	Yes
Monitoring instrument calibration	No	Yes
Comments on monitoring results	No	Yes

Qualifier Description
 This table contains the definitions for the data qualifiers.

Table Name Description

Entity Name	Key Field?	Nulls Allowed?
Data qualifier code	Yes	No
Qualifier description	No	No
Comments on qualifier	No	Yes

References
 This table contains the complete reference citation for sample data, analysis, results, and physical and chemical properties. This table describes a reference with enough information to obtain the source from an information repository (such as the Office of Scientific and Technical Information or the publisher).

Entity Name	Key Field?	Nulls Allowed?
Reference id	Yes	No
Reference type	No	No
Accessible to public	No	Yes
Authors	No	No
Year published	No	No
Reference title	No	No
Document number	No	Yes
Publisher	No	Yes
Publisher city	No	Yes
Publisher state	No	Yes
Publisher country	No	Yes
Comments on reference	No	Yes

Result Average
 This table contains simple statistical values for analytical results which are not flagged as "suspect" (designated as "S" in the data qualifier code field). Statistics are based on values as displayed in the Analysis Results table, and may differ slightly from reported averages due to round-off errors.

Table Name**Description**

Entity Name	Key Field?	Nulls Allowed?
Result average id	Yes	No
Tank id	No	No
Sample job number	No	No
Sample date	No	No
Chemical id	No	No
Result average	No	Yes
Result standard deviation	No	Yes
Reporting limit	No	Yes
Units	No	No
Number of sample results	No	Yes
Data qualifier code	No	Yes
Sample device	No	No
Laboratory abbreviation	No	No

Sample Data

This table contains information about the conditions under which the sample was collected and the type of sample that was taken.
This information is generally taken from published reports.

Table Name Description

Entity Name	Key Field?	Nulls Allowed?
Collection id	Yes	No
Sample id	No	Yes
Tank id	No	Yes
Tank riser	No	Yes
Tank temperature	No	Yes
Tank pressure	No	Yes
Date-time of sample	No	No
Sample device	No	No
Sampling method	No	No
Comments on sampling	No	Yes

Sample-Reference Relation
 This table relates sample and reference information. This table connects the documents that relate to a sampling event, including sample plans, work packages, and post-sampling reports, with the sampling event.

Entity Name	Key Field?	Nulls Allowed?
Collection id	Yes	No
Reference id	Yes	No

Unit Conversion

Entity Name	Key Field?	Nulls Allowed?
Result id	Yes	Yes
Converted result	No	No
Converted units	Yes	No
Conversion method	No	Yes

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
Analysis date	Date of sample analysis.	09-09-1993 11:44	Analysis Results	No	Yes	datetime
Analysis method	Primary instrumentation used to analyze a sample (a sample is defined as a discrete quantity of material collected for analysis). If the analysis does not involve a specific instrument (for example, gravimetric analysis), then a general description is reported.	GC/FID TO-14 CGM OVA colorimetric tube	Analysis Method Description	Yes	No	varchar 50
Analysis method name	Description of the method used to analyze the sample	Gas chromatograph with flame ionization detector. Combustible gas meter uses a catalytic bead detector to measure fuel content in air as %LFL.	Analysis Results	No	No	varchar 50
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. Birn, P. R. Seesing EPA Anonymous	Monitoring Results	No	No	varchar 50
			Analysis Method Description	No	No	varchar 255
			References	No	No	varchar 255

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Basis of holding time	Basis of specified allowed holding time. Specifies whether allowed holding time was based on administrative requirements or on laboratory validated holding times, and provides holding time reference. The references are WHC-SD-WM-CAPP-013, ORNL-CASD-FR-241TY103.95 Rev.1, and PNL-10873.	Administratively required by doc. num. WHC-SD-WM-QAPP-013. Study described in doc. num. PNL-10873. Study described in doc. num. ORNL-CASD-FR-241TY103.95 Rev.1.	Analysis Results	No	Yes	varchar 100
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 In-house developed code that uniquely identifies a chemical.	67-66-3 109-79-5 UAK014-02	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
			Flammability Data	Yes	No	char 15
			Flammability Results	No	No	char 15
			Result Average	No	No	char 15
Chemical name	Standard and synonymous names of a chemical.	Hexane Hexyl hydride	Chemical Name Description	Yes	No	varchar 240

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	950412142342	Analysis Results	No	No	char 12
Comments on monitoring data	Any concerns or unusual information about the monitoring event.	to be defined	Monitoring Data	No	Yes	varchar 255
Comments on monitoring results	Any concerns or unusual information about the results		Monitoring Results	No	Yes	varchar 255
Comments on qualifier	Basis of qualifier.	Based on EPA contract laboratory protocol.	Qualifier Description	No	Yes	varchar 255
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

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
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
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
Data qualifier code	Single-letter flags that indicate noteworthy aspects of sample result. For the Tank Vapor Database, some of the qualifiers are: U - compound was analyzed for but not detected above reporting value. J - reported concentration was estimated. B - compound found in associated laboratory blank as well as sample. E - reported concentration was above the instrumental calibration range. N - compound was tentatively identified. H - analysis was performed after allowed analytical holding time had elapsed or analysis date is not available. X - analytical laboratory did not have approved quality assurance documentation, or a significant quality assurance deficiency was associated with reported result. S - result suspect - see comment field.	UH J	Analysis Results	No	Yes	char 10

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Data qualifier code	<p>Single-letter flags that indicate noteworthy aspects of sample result. For the Tank Vapor Database, some of the qualifiers are:</p> <p>U - compound was analyzed for but not detected above reporting value.</p> <p>J - reported concentration was estimated.</p> <p>B - compound found in associated laboratory blank as well as sample.</p> <p>E - reported concentration was above the instrumental calibration range.</p> <p>N - compound was tentatively identified.</p> <p>H - analysis was performed after allowed analytical holding time had elapsed or analysis date is not available.</p> <p>X - analytical laboratory did not have approved quality assurance documentation, or a significant quality assurance deficiency was associated with reported result.</p> <p>S - result suspect - see comment field.</p>	UH J	Monitoring Results	No	Yes	char 10
Date-time of monitoring	Date and time that the monitoring was performed.	09-09-1997 12:34	Qualifier Description	Yes	No	char 10
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	Result Average	No	Yes	char 10
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	Monitoring Data	No	No	datetime
			Sample Data	No	No	datetime
			References	No	Yes	varchar 30

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Elapsed hold time	Time in days between sample collection and sample analysis.	15	Analysis Results	No	Yes	int
Flammability result id	System-generated code used to make each flammability result record unique. This code is internal to the database and should not be used for tracking results.	961011062416	Flammability Results	Yes	No	char 12
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
Holding time	Allowed time in days between sample collection and sample analysis. Value given is the shorter of any administratively specified or published laboratory analytical holding time study criteria.	30	Analysis Results	No	Yes	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	Result Average	No	No	char 6
Laboratory name	Name of laboratory performing analyses	Pacific Northwest National Laboratory Oak Ridge National Laboratory	Laboratory Description	No	Yes	varchar 30
			Laboratory Description	No	Yes	char 14
			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
LFL	Lower flammability limit of identified analytes in air at standard temperature and pressure	50000	Flammability Data	Yes	No	int
LFL units	Units of lower flammability limit	ppmv	Flammability Data	No	No	char 10
Measurement type	Type of measurement reported	Flammability Percent Oxygen Organic vapor concentration Ammonia concentration	Monitoring Results	No	No	varchar 45
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
Monitoring data id	System-generated code used to make each monitoring data record unique. This code is internal to the database and should not be used for tracking monitoring activities.	960911051625	Monitoring Data	Yes	No	char 12
Monitoring instrument calibration	Method used to calibrate monitoring instrument	to be defined	Monitoring Results	No	No	char 12
Monitoring instrument model	Model designation of monitoring instrument	TMX-	Monitoring Results	No	Yes	varchar 45
Monitoring result id	System-generated code used to make each monitoring results record unique. This code is internal to the database and should not be used for tracking results.	960911055014	Monitoring Results	Yes	No	char 12

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

Number of sample results	Number of sample results used in "result average".	3 2 0	Result Average	No	Yes	Int
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
Percent LFL	Result average times 100 divided by the lower flammability limit of the analyte	0.7 2.1	Flammability Results	No	No	float
Probe depth	Distance in meters from top face of the riser flange to the instrument inlet.	3	Monitoring Data	No	No	Int
Publisher	Name of company that printed the reference	Pacific Northwest Laboratory Seasing & Grove, Inc.	References	No	Yes	varchar 255
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

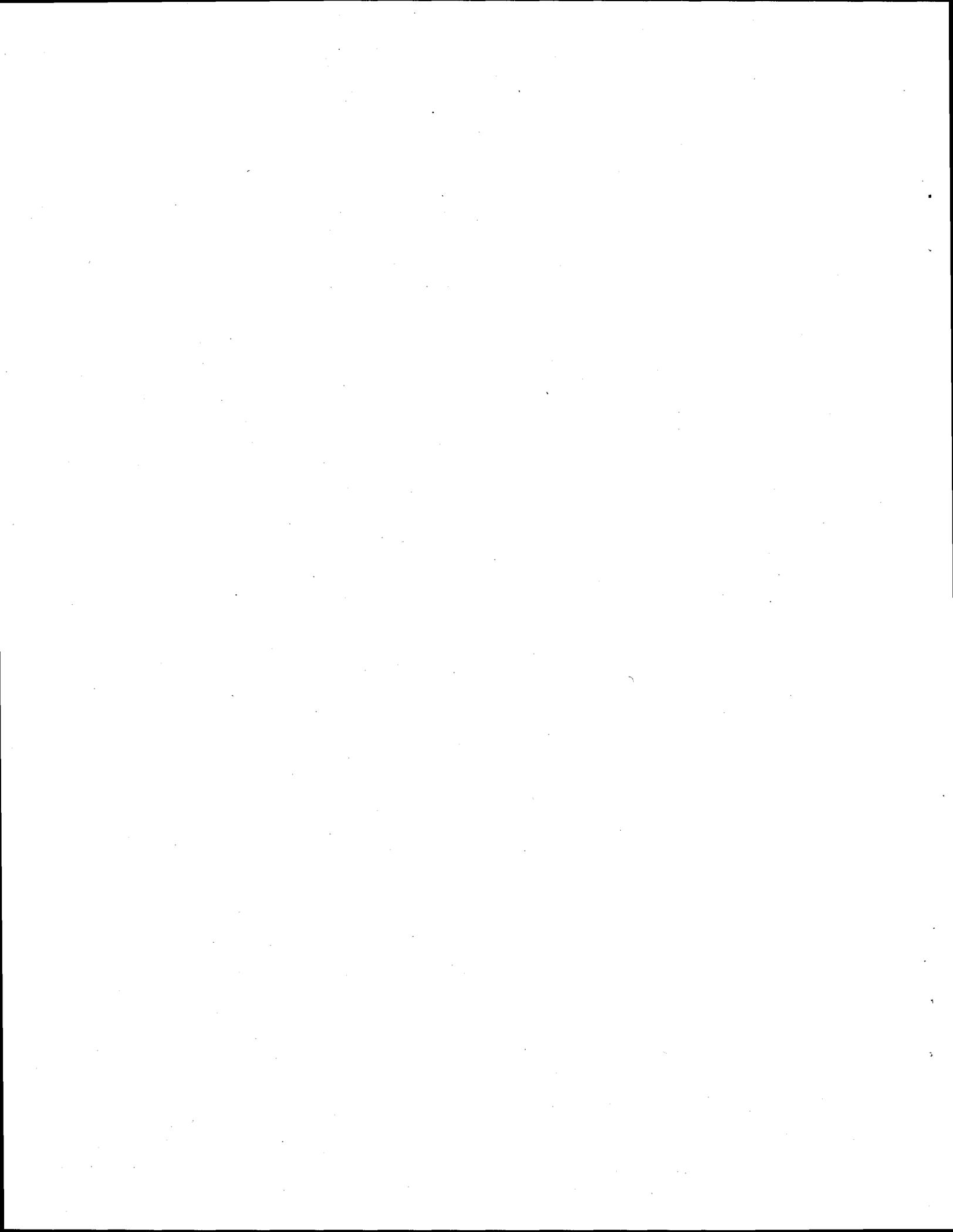
Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Qualifier description	Definition for the data qualifier code.	'H'- Indicates analysis was performed after allowed analytical holding time had elapsed or analysis date is not available.	Qualifier Description	No	No	varchar 255
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	950123123148	Analysis Results	No	No	char 12
			Flammability Data	No	No	char 12
			Monitoring Data	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
Reporting limit	A lower limit below which the concentration of a constituent is not reported. The concentration of the constituent either cannot be measured or is below an instrument detection limit or below a contract required quantitation limit. This is a text field and cannot be included in numerical calculations. For more information on reporting limits, see the corresponding references	< 0.04	Analysis Results	No	Yes	char 20
Result average	Arithmetic mean of all results for an identified analyte which are not flagged as "suspect" in the data qualifier code field. The result average is specific for the tank, sample job #, sample device, and analytical laboratory.	0.5 204 0.0024	Monitoring Results Result Average	No No	Yes Yes	char 20 char 20
Result average id	System-generated code used to make each average result record unique. This code is internal to the database and should not be used for tracking results.	961011062416	Flammability Results	No	No	char 12
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.	950823114503	Result Average Analysis Results	Yes Yes	No No	char 12 char 12
			Unit Conversion	Yes	Yes	char 12

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Result standard deviation	Standard deviation of all nonsuspect results for identified analyte, as given by the following formula: Square Root of (the sum of the squares of the deviations from the average] divided by (n-1).	0.0022	Result Average	No	Yes	float
Result value	The estimated or quantified concentration of a chemical.	13.55	Analysis Results	No	Yes	float
Sample date	Date the sample was taken (a sample is defined as a discrete quantity of material collected for analysis)	9/9/1993	Monitoring Results	No	Yes	float
Sample device	Description of the type of container used to collect a sample (a sample is defined as a discrete quantity of material collected for analysis).	SUMMA canister OVS tube	Result Average	No	No	char 20
Sample id	Code assigned to a sample by the collecting organization (a sample is defined as a discrete quantity of material collected for analysis)	S6014-A24.531	Sample Data	No	Yes	varchar 45
Sample job number	Reference number of sampling job assigned by sample collecting organization. This number is the first 5 characters of the Sample Id. An example is S6014 of S6014-A24.531.	S6052 S4009	Flammability Results	No	No	char 6
			Result Average	No	No	char 6

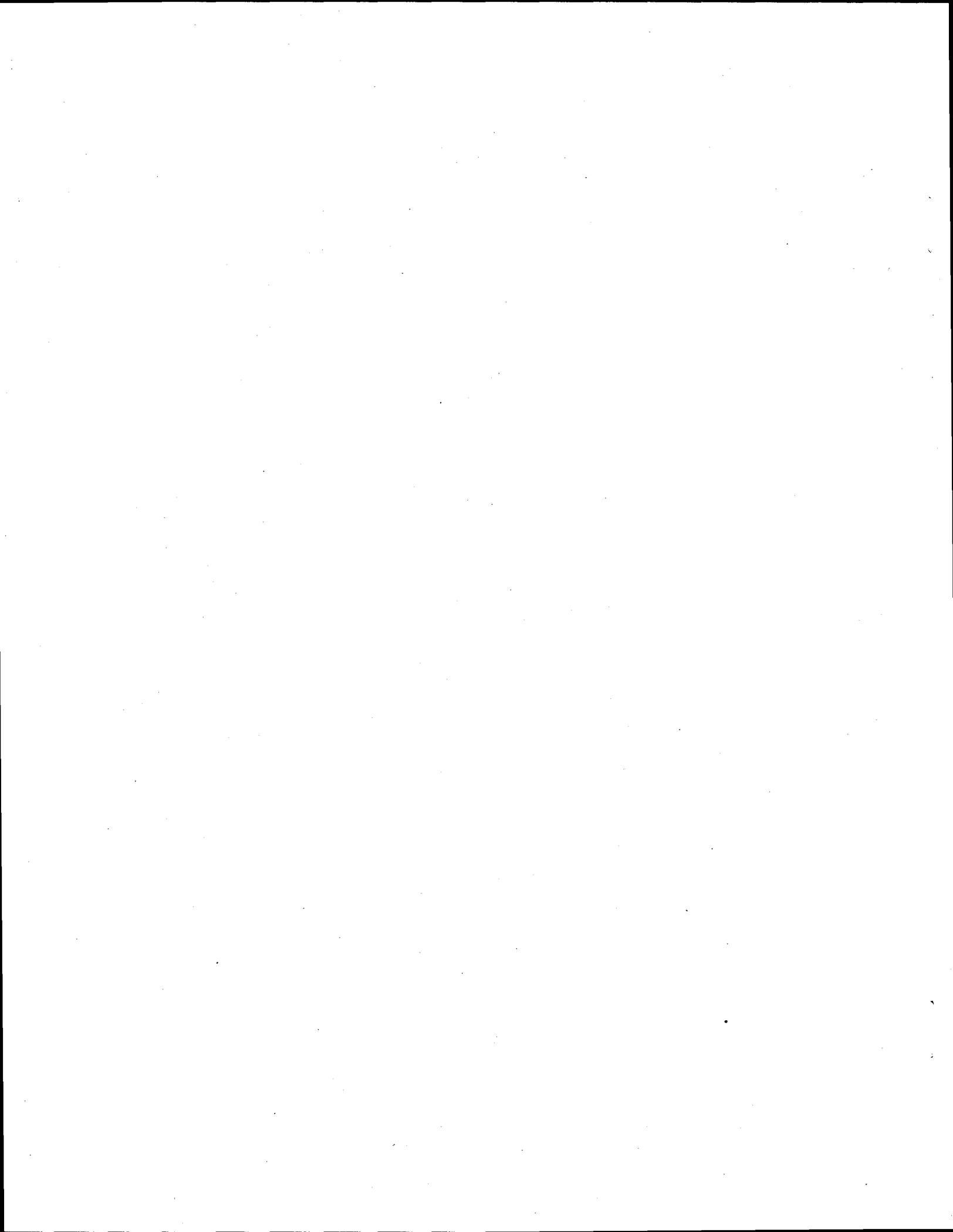
Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Sampling method	Description of the type of general method used to collect a sample (a sample is defined as a discrete quantity of material collected for analysis)	ISS VSS ISVS w filter ISVS wo filter	Sample Data	No	No	char 20
Structure-formula	Condensed structural notation for a chemical.	C2H4O	Chemical Id Description	No	Yes	varchar 255
Tank id	Code that identifies each tank in a tank farm system	241-C-103 241-SY-101	Flammability Results	No	No	char 15
			Monitoring Data	No	No	char 15
			Result Average	No	No	char 15
			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	Monitoring Data	No	No	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

Entity Name	Description	Examples	Table Name	Key Field?	Can be Null?	Type/Length
Units	Units used to measure the result value or the reporting limit. Results are not adjusted for presence of water vapor. Mass/Volume results are for 273.15 K and 760 torr conditions.	mg/L L %	Analysis Results	No	No	char 10
			Monitoring Results	No	No	char 10
			Result Average	No	No	char 10
Year published	Year the reference was published according to the title page	1994	References	No	No	char 4



Appendix G

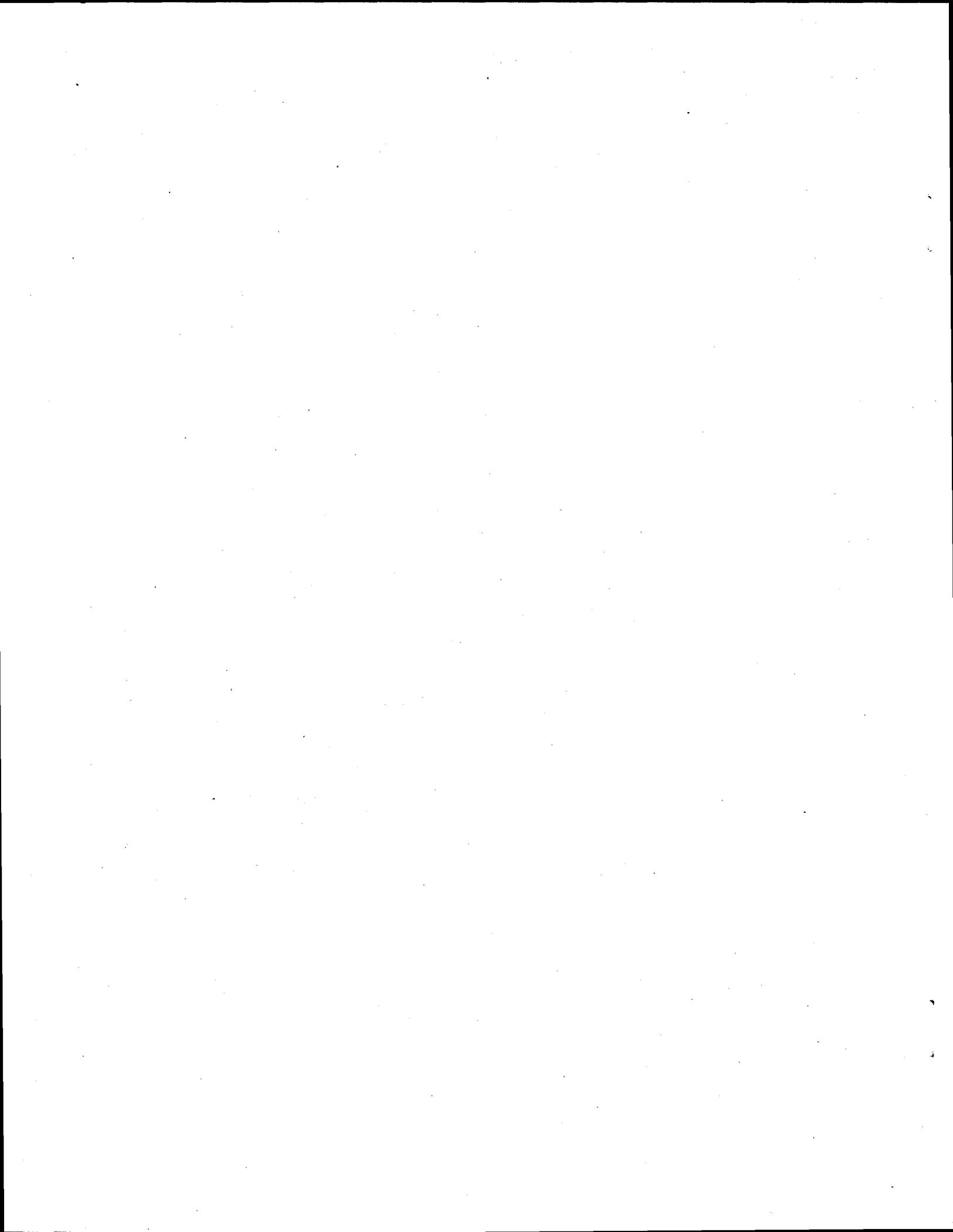
Data Qualifiers



Appendix G

Data Qualifiers

Data Qualifier Code	Data Qualifier Description	Comments
B	Compound found in associated laboratory blank as well as sample	Based on EPA contract laboratory protocol
E	Reported concentration was above the instrumental calibration range	Based on EPA contract laboratory protocol
H	Analysis was performed after allowed analytical holding time had elapsed or analysis date is not available	Chosen by the tank vapor database (TVD) staff unique to TVD
J	Reported concentration was estimated	Based on EPA contract laboratory protocol
N	Compound was tentatively identified	Based on EPA contract laboratory protocol
S	Result suspect - see comment field	Chosen by the tank vapor database (TVD) staff unique to TVD
U	Compound was analyzed for but not detected above reported value	Based on EPA contract laboratory protocol
X	Analytical laboratory did not have approved quality assurance documentation, or that a significant quality assurance deficiency was associated with reported result	Chosen by the tank vapor database (TVD) staff unique to TVD



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