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Program Plan for the Resolution of Tank Vapor Issues

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Office of Environmental Restoration and
Waste Management

**Westinghouse
Hanford Company**

P.O. Box 1970
Richland, Washington

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EXECUTIVE SUMMARY

Since 1987, workers at the Hanford Site waste tank farms in Richland, Washington, have reported strong odors emanating from the large, underground high-level radioactive waste storage tanks. Some of these workers have complained of symptoms (e.g., headaches, nausea) related to the odors.

In 1992, the U.S. Department of Energy, which manages the Hanford Site, and Westinghouse Hanford Company determined that the vapor emissions coming from the tanks had not been adequately characterized and represented a potential health risk to workers in the immediate vicinity of the tanks. At that time, workers in certain areas of the tank farms were required to use full-face, supplied-breathing-air masks to reduce their exposure to the fugitive emissions. While use of supplied breathing air reduced the health risks associated with the fugitive emissions, it introduced other health and safety risks (e.g., reduced field of vision, air-line tripping hazards, and heat stress).

In 1992, an aggressive program was established to assure proper worker protection while reducing the use of supplied breathing air. This program focuses on characterization of vapors inside the tanks and industrial hygiene monitoring in the tank farms. If chemical filtration systems for mitigation of fugitive emissions are deemed necessary, the program will also oversee their design and installation.

This document presents the plans for and approach to resolving the Hanford Site high-level waste tank vapor concerns. It is sponsored by the Department of Energy Office of Environmental Restoration and Waste Management.

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LIST OF TERMS

AIHA	American Industrial Hygiene Association
ASME	American Society of Mechanical Engineers
CES	Consensus Exposure Standard
CGM	Combustible Gas Meter
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy, Richland Field Office
DQO	Data Quality Objective
DST	Double-Shell Tank
ECC	Emergency Control Center
EPA	U.S. Environmental Protection Agency
EPA TO method	EPA Toxic Organic Analysis Method
FAS	Field Analytical Services
FeCN	Ferrocyanide $[\text{Fe}(\text{CN})_6]^-$
FID	Flame Ionization Detector
FSA	Field Sampling and Analysis
FTIR	Fourier Transform Infrared Spectrophotometer
FY	Fiscal Year
GC	Gas Chromatograph
GC/FID	Gas Chromatograph/Flame Ionization Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
HCN	Hydrogen Cyanide
HEHF	Hanford Environmental Health Foundation
HEPA	High Efficiency Particulate Air (Filter)
IH	Industrial Hygiene
kgal	Kilogallon (Thousand Gallon)
LFL	Lower Flammability Limit
Mgal	Megagallon (Million Gallon)
MS	Mass Spectrometer
NFPA	National Fire Protection Association
NISI	Northwest Instrument Systems, Inc.
NOAS	Noxious Odor Advisory System
NPH	Normal Paraffin Hydrocarbons
OGI	Oregon Graduate Institute
ORNL	Oak Ridge National Laboratories
OSHA	Occupational Safety and Health Administration
PNL	Pacific Northwest Laboratory
PPE	Personal Protective Equipment
Program Plan	Program Plan for the Resolution of Tank Vapor Issues
PUREX	Plutonium Uranium Extraction
QA	Quality Assurance
QAM	Quality Assurance Manual

LIST OF TERMS (continued)

QAP	Quality Assurance Plan
SNL	Sandia National Laboratories
SST	Single-Shell Tank
TAP	Tank Advisory Panel
TBP	Tributyl Phosphate
TPA	Tri-Party Agreement
TRP	Toxicology Review Panel
TWRS	Tank Waste Remediation Systems
TWA	Time Weighted Average
USQ	Unreviewed Safety Question
Vapor Program	Tank Vapor Issue Resolution Program
VCC	Vapor Conference Committee
VOC	Volatile Organic Compound
VSS	Vapor Sampling System
WBS	Work Breakdown Structure
WHC	Westinghouse Hanford Company
WHC/ESQ	WHC Emergency, Safety, and Quality
WTSP	Waste Tank Safety Programs
WTSS	Waste Tank Safety Support

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PROGRAM PLAN FOR THE RESOLUTION OF TANK VAPOR ISSUES

1.0 INTRODUCTION

The Tank Vapor Issue Resolution Program was established in 1992 to resolve the health and safety issues related to noxious gases and vapors associated with the high-level radioactive waste storage tanks at the Hanford Site. These issues stem from: 1) a history of exposures of tank farm personnel to unknown levels of noxious gases and vapors; and 2) the concern that until the gases and vapors in the waste tanks are well characterized, the true health and safety risks cannot be assessed. For brevity in this document, the term "vapors" shall refer to both gases and vapors.

1.1 PURPOSE

This program plan describes the background, priorities, strategy, logic, methods and task descriptions needed to resolve health and safety issues associated with headspace vapors from the Hanford Site high-level radioactive waste storage tanks. The plan also describes the approach of the Tank Vapor Issue Resolution Program (Vapor Program). A methodology for resolving the vapor issues for waste tank 241-C-103 is developed and applied in this plan; appropriate elements of this methodology will be applied to other waste tank vapor issues.

1.2 SCOPE

This program plan describes the efforts of Westinghouse Hanford Company (WHC) Tank Waste Remediation Systems (TWRS) to characterize the waste tank headspace vapors and to understand the impact of these vapors if they migrate into the workers' breathing zone. Efforts of Westinghouse Hanford Company/Emergency, Safety and Quality (WHC/ESQ) to evaluate industrial hygiene issues associated with the waste tank vapors are also discussed. Initiatives to resolve a related safety issue, the potential flammability of vapors and an aerosol in tank 241-C-103, are also described.

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2.0 BACKGROUND

2.1 GENERIC WASTE TANK DESIGN

High-level radioactive waste generated by processes at the Hanford Site has been stored since the mid-1940s in large, underground storage tanks. These waste tanks are located in the 200 East and 200 West areas of the Site, and are grouped physically in tank farms. Due to the variety of waste-generating processes at the Hanford Site and the range of waste types stored in the tanks, the history and current inventory of each waste tank are unique.

The Hanford Site contains 149 large, single-shell tanks (SSTs), constructed between 1943 and 1964, that contain waste generated between 1944 and 1972. The SSTs are all of the same basic construction, and have waste capacities of 1.9, 2.8, or 3.8 ML (0.53, 0.76, or 1.0 Mgal) (Figure 2-1). They are 13.7 m (75 ft) in diameter, and measure approximately 9, 11, or 13 m (30, 37, or 44 ft) from the top of the curved tank ceiling to the tank bottom, depending on their waste capacity. The tanks are constructed of reinforced concrete designed to support the weight of the soil (typically about 2 m [7 ft]) that covers the tanks, as well as the hydraulic loads of the waste itself. The waste-bearing surfaces are lined with non-stress-relieved carbon steel having a typical thickness of 1.27 to 2.54 cm (0.5 to 1.0 in.).

There are 28 double shell tanks (DSTs) at the Hanford Site, all constructed since 1964. DSTs are similar to SSTs, being 13.7 m (75 ft) in diameter, and approximately 14.6 m (48 ft) from the tank bottom to the domed ceiling (Figure 2-2). Each DST has a waste storage capacity of 4.4 ML (1.16 Mgal). DSTs, unlike SSTs, have a primary, stress-relieved carbon steel tank inside a steel-lined, reinforced-concrete shell. All 28 Hanford Site DSTs are currently considered to be "in-service" tanks, although 5 are prohibited from receiving waste due to their potential for hydrogen gas generation (Hanlon 1994). All the DSTs are actively ventilated to limit the build-up of flammable or noxious vapors; for this reason, the focus of the Vapor Program will be limited initially to the SSTs.

2.2 STATEMENT OF THE GENERIC VAPOR PROBLEM FOR SINGLE-SHELL TANKS

Are tank farm workers being exposed to potentially hazardous chemical constituents from waste tanks at levels that exceed established guidelines?

2.3 STATEMENT OF THE SPECIFIC VAPOR PROBLEM FOR TANK 241-C-103

A number of people have reported ill effects, including headache, burning sensation in nose and throat, nausea, and impaired pulmonary function, while working around waste tanks on

- 149 tanks constructed 1943-64
- Bottom of tanks at least 50 m (150 ft) above groundwater
- No waste added to tanks since 1980
- Tanks currently contain
 - ~140,000 m³ (37 Mgal) of saltcake, sludge, and liquid
 - ~ 555 x 10¹⁶ Bq (150 MCi)
 - 67 are assumed to have leaked ~ 3,800 m³ (1 Mgal)

Figure 2-1. Single-Shell Tank Design.

29305036.1

- 28 tanks constructed between 1968-86
- 3,785 m³ to 4,315 m³ (1 to 1.14 Mgal) capacity
- Tanks currently contain
 - ~ 9 x 10⁴ m³ (24 Mgal) of mostly liquids (also sludges and salts)
 - ~400 x 10¹⁶ Bq (110 MCi)
- None have leaked

Figure 2-2. Double-Shell Tank Design.

the Hanford Site. As indicated in the *Program Plan for the Resolution of Tank Vapor Issues*, WHC-EP-0562 (Osborne 1992), musty and foul odors, including the smell of ammonia, have been reported emanating from several SSTs. During the period between July 1987 and May 1992, 16 complaints of exposures to odors were reported, involving 27 workers. Ten of these occurrences, involving 18 workers, were linked to the 241-C tank farm. In particular, tank 241-C-103 was implicated in six of the reported occurrences.

For a period of 33 years (1946-1979), tank 241-C-103 received about 30 types of waste from various sources, both directly and as a receiving tank in a tank cascade (Jungfleisch 1987, Carothers 1988). According to Jungfleisch, the wastes added to tank 241-C-103 included wastes generated from four primary recovery processes, two secondary recovery processes, evaporators, in-tank solidification processes, semi-works operations, decontamination operations, N Reactor, Pacific Northwest Laboratory (PNL), and both in-process and in-tank waste scavenging. Tank 241-C-103 was also an accumulator tank for metal waste from other tanks (before processing for uranium recovery) and for supernatants from other tanks (before processing for cesium recovery). Data on N Reactor waste and PNL waste was lacking because of the then-proprietary nature of those operations. However, it is likely that tank 241-C-103 contains tributyl phosphate (TBP), normal paraffinic hydrocarbons (NPH), and various radiation-induced degradation products.

After July 1979, no wastes were transferred into or out of tank 241-C-103. At present, tank 241-C-103 is designated as an organic tank and is on the Organic Watch List (Strachan et al. 1993). Hanlon (1994) estimated that the tank contained 234,695 L (62,000 gal) of sludge and 503,458 L (133,000 gal) of aqueous supernatant liquids. Additionally, between 3.8 and 5 cm (1.5 and 2.0 in.) of organic liquid cover the waste surface. This organic liquid is composed principally of TBP and NPH.

Reports of illness experienced by people working near tank 241-C-103 have led to a need to determine if the symptoms are related to material coming from the tank. This determination involves a number of steps, including: (1) analysis of material in the tank headspace to establish maximum concentrations of materials available for release from the tank; (2) analysis of volatile materials released through the high-efficiency particulate air (HEPA) filter on the tank exhaust port; (3) determination of routes and levels of fugitive emissions from the tank; (4) evaluation of the toxicologic potential (including the exposure potential) of the headspace constituents and the materials released from the tank; (5) area monitoring; and (6) breathing zone monitoring.

When sufficient data has been obtained for the above areas, it will be possible to determine what, if any, control and monitoring measures are necessary. In the interim, WHC/ESQ has adopted the American Industrial Hygiene Association (AIHA) sampling strategy (AIHA 1991) to monitor personnel exposure to tank farm vapors. The sampling results will be used to ensure workers' protection in and around the tank farm area. As additional in-tank characterization of analytes of toxicologic interest are identified by the Toxicology Review Panel (TRP), the air sampling approach will be reassessed.

2.4 STATEMENT OF THE SPECIFIC FLAMMABILITY PROBLEM FOR TANK 241-C-103

The concern that a flammability hazard exists in tank 241-C-103 arises from two possible scenarios. First, the layer of organic liquid could potentially ignite and result in a "pool" fire. Second, if a very dense aerosol composed primarily of organic droplets exists, the available fuel in the headspace could support flame propagation in upper regions of the headspace. Either scenario could result in an increase in the pressure within the tank, a breach of the tank, and subsequent release of radiological contamination to the atmosphere and/or the ground. Since the risk and potential damage of a fire in tank 241-C-103 have not been thoroughly evaluated, the presence of the organic liquid layer in the tank has been declared an unreviewed safety question (USQ). Resolution and closure of this organic layer "pool" fire USQ are outside the scope of the Vapor Program, and are the responsibilities of the Organic Program.

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3.0 THE TANK VAPOR SAFETY PROGRAM

3.1 OBJECTIVES

The objectives of the Tank Vapor Safety Program are:

- Ensure a safe work environment in the tank farms.
- Select, modify, and validate a vapor analysis methodology that will allow the chemical characterization needed to accomplish the goals of the Vapor Program.
- Ensure that the sampling and analysis technologies selected, modified, validated, and used to resolve vapor issues are available for transfer to the Hanford Site. These methods can then be applied to characterize the waste tank headspaces.
- Identify constituent gas phase components in the tank headspace and assess the potential for worker exposure to air contaminants from this source term.
- Resolve the vapor flammability concern for tank 241-C-103.
- Identify a path that will: (1) provide a safe work environment that does not require routine use of supplied air; and (2) allow relaxation of supplied air restrictions that currently exist in tank farms.
- Support implementation of a tank farm-specific health and safety plan (to include area air monitoring) which conforms to the requirements of 29 CFR 1910.120.
- Recommend administrative controls based on alarmed monitoring systems and worker observations as outlined in the tank farm-specific health and safety plan.
- Recommend engineered monitoring and treatment systems that will reduce the emission of potentially toxic vapors from waste tanks in a cost-effective and timely manner.
- Comply with U.S. Department of Energy (DOE) orders, federal and state laws, and legal agreements pertinent to the vapor issues.

While it is the objective of this program plan to pursue engineered systems (as applicable) to control health effects caused by fugitive vapor emissions, these methods may not and need not remove all odors.

The treatment system (if required) that is selected will reduce the concentrations (measured at the system effluent port) of all specified gases and vapors to below their consensus exposure standards (CES) at the system effluent port.

The ultimate and primary goal of the Tank Vapor Safety Program is to provide a safe work environment that minimizes the use of supplied-air respiratory protection in the tank farms. The Program will also address the requirement to use supplied air in support of work procedures for intrusive activities in and around the waste tanks.

3.2 PRIORITIES

Public Law 101-510, Section 3137, *Safety Measures for Waste Tanks at Hanford Nuclear Reservation*, commonly known as the Wyden Amendment, defines a Priority 1 safety issue as any issue or situation having the potential to result in onsite worker or offsite radiation exposure through an uncontrolled release of fission products. Although the waste tank vapor issues are not specifically identified on the Wyden Amendment Priority 1 list, WHC has upgraded the tank vapor issues to its Priority 1 list. Consequently, all work being conducted by the Vapor Program in fiscal year (FY) 1994/95 is classified as Priority 1 work.

3.3 PROGRAM DRIVERS

The following requirements, regulations, orders, standards, and sources are drivers for the Vapor Program:

3.3.1 Employee Sources

- Information from employees
- Employee concerns

3.3.2 Code of Federal Regulations

The following Federal regulations are drivers for the Tank Vapor Program:

- 29 CFR 1910.1000, *OSHA Permissible Exposure Levels* (29 CFR 1910)
- 29 CFR 1910.1200, *OSHA Hazard Communication Standard* (29 CFR 1910)
- 29 CFR 1910.120, *Hazardous Waste Operations and Emergency Response* (29 CFR 1910)

3.3.3 Atomic Energy Act of 1954

The following DOE/DOE-RL orders are major drivers for the Tank Vapor Program:

- Atomic Energy Act of 1954 (DOE 1954)
- DOE Order 5480.8A, *Contractor Occupational Medical Program* (DOE 1992)
- DOE RLIP 5480.10, *Contractor Industrial Hygiene Program* (DOE-RL 1990)
- DOE Order 5480.10, *Contractor Industrial Hygiene Program* (DOE 1985)
- DOE Order 5480.1B, *ES&H Program for DOE Operations* (DOE 1993)
- DOE Order 5480.4, *Environmental Protection, Safety, and Health Protection Standard* (DOE 1984)
- DOE Order 5700.6C, *Quality Assurance* (DOE 1991)
- DOE RLIP 5480.4C, *Environmental Protection, Safety, and Health Protection Standard for RL* (DOE-RL 1992)
- RLIP 5480.8, *Contractor Occupational Medical Program* (DOE-RL 1994)
- DOE Order 5483.1A, *Occupational Safety and Health Programs for DOE Contractor Employees at Government-Owned/Contractor-Operated Facilities* (DOE 1983)
- DOE RLIP 5483.1B, *Occupational Safety and Health Programs for DOE Contractor Employees at Government-Owned/Contractor-Operated Facilities* (DOE-RL 1989)

3.3.4 Other Drivers

- American Conference of Governmental Industrial Hygienists (ACGIH) Handbook, *Threshold Limit Values and Biological Exposure Indices* (ACGIH 1993-94)
- National Institute of Safety and Health (NIOSH) Recommended Exposure Levels (NIOSH 1993)
- WHC-EP-0774, Tank 241-C-103 Vapor and Gas Sampling Data Quality Objectives (Osborne et al. 1994a)

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- WHC-SD-WM-DQO-002, Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution (Osborne et al. 1994b)
 - WHC-SD-WM-SP-003, Rotary Core Sampling Data Quality Objective (Price 1994)
 - National Fire Protection Association (NFPA) 1, *Fire Prevention Code* (NFPA 1992a)
 - NFPA 30, *Flammable and Combustible Liquids Code* (NFPA 1993a)
 - NFPA 54, *National Fuel Gas Code*, (NFPA 1992b)
 - NFPA 55, *Compressed and Liquefied Gases in Portable Cylinders* (NFPA 1993b)
 - NFPA 70, *National Electrical Code* (NFPA 1993c)
 - NFPA 72, *National Fire Alarm Code* (NFPA 1993d)
 - NFPA 77, *Static Electricity* (NFPA 1993e)
 - NFPA 79, *Electrical Standards for Industrial Machinery* (NFPA 1991)
 - NFPA 101, *Safety of Life from Fire in Buildings and Structures* (NFPA 1994)

3.3.5 TWRS Safety Initiatives

A number of significant safety issues associated with Hanford Site tank waste have been identified (O'Leary 1993). Specifically, these include the release of potentially toxic vapors. The five safety initiatives associated with toxic vapor issues are:

- 2i - Resolve flammability issues associated with tank 241-C-103 by January 31, 1994.
- 2m - Sample and characterize tank vapors from tank 241-C-103 by June 1994.
- 2n - Complete engineering evaluation of alternatives for treatment of tank 241-C-103 vapor space by June 1994.
- 2o - Sample and characterize remaining suspect tanks by June 1995.
- 2p - Provide vapor monitoring equipment with alarm capability and/or ventilation upgrades to tanks where warranted, by April 30, 1997.

3.3.6 Washington State Administrative Code

Waste Tank Safety Programs activities must comply with the State of Washington Administrative Codes (WAC) with respect to managing dangerous waste. The specific regulation is WAC 173-303, *Dangerous Waste Regulations*, Section 110, "Sampling and Testing Methods" (WAC 173-303).

3.3.7 Defense Nuclear Facilities Safety Board (DNFSB)

The DNFSB was created to provide advice and formal recommendations to the President of the United States and to the Secretary of Energy regarding public health and safety issues at DOE nuclear facilities. The DNFSB reviews operations, practices, and occurrences at DOE nuclear facilities and makes appropriate health and safety recommendations. If any aspect of operations, practices, or occurrences reviewed by the DNFSB is determined to present an imminent or severe threat to public health or safety, the DNFSB transmits its recommendations directly to the President.

3.3.8 Tri-Party Agreement

The *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement [TPA]) (Ecology et al. 1990) contains provisions governing the treatment, storage and disposal of hazardous waste, including remedial and corrective action activities. During 1993, new negotiations were conducted by DOE, U.S. Environmental Protection Agency (EPA), and Washington State Department of Ecology. New milestones were negotiated and a reduced set of specifications for characterization requirements was adopted (Ecology et al. 1994). The specific tank vapor TPA milestones are:

- M-40-06 Complete vapor sampling and characterization of tank 241-C-103 by August 30, 1994.
- M-40-08 Complete vapor sampling and characterization of all Organic Watch List tanks by November 1995.
- M-40-03 Complete vapor sampling and characterization of all Ferrocyanide Watch List tanks by November 1995.
- M-40-07 Commence operation of vapor treatment system on tank 241-C-103 by June 1995.

3.4 PROGRAM OVERVIEW

3.4.1 Program Elements and Scope

Overall resolution of vapor issues requires a multi-faceted strategy that includes such diverse projects as:

- Qualitative and quantitative characterization of vapors in the tank headspace.
- An evaluation of the potential mechanisms for release of vapors from waste tanks.
- Worker exposure profiles.
- Accumulation of occupational vapor exposure data.
- Toxicological impact assessments.
- Development of criteria for administrative controls.
- Evaluation of engineering alternatives for viable engineering controls.
- Development of a tank vapor flow monitor device with alarming capability.
- Development of a database system for communicating vapor information.

These projects are all essential pieces of the complex matrix of information needed for resolution of vapor issues.

Essential tools needed to gather this information include: (1) development of a Vapor Sampling System (VSS); (2) implementation of the Noxious Odor Advisory System (NOAS) program to allow for timely and effective investigation of all future vapor exposure incidents; and (3) creation of a sound, baselined, industrial hygiene (IH) program to ensure that worker safety in a chemical environment is well understood and controlled. The centerpiece of the IH program is the implementation of the 29 CFR 1910.120 guidelines via the Health and Safety Plan.

Worker safety at the Hanford Site is of paramount importance. Until tank vapors are well characterized and emissions are controlled, personal protective equipment (PPE) will be a necessary element of the IH program. However, the goal of the entire Tank Vapor Safety Program is to minimize dependence upon this interim protective measure.

3.4.2 Tank Headspace Characterization

Resolution of tank vapor issues will require development of a vapor characterization methodology. The strategy is to employ a phased approach to resolving the technical problems associated with tank vapor characterization.

The overall goal of waste tank vapor characterization activities has been broken down into logically distinct phases, with the tasks and goals of each phase being in part determined by the success and results of previous phases. Figure 3-1 illustrates the logic of this phased approach. Phases 1 and 2, discussed here and later in the program plan, are analytical, scientific, and/or engineering development phases with the goal of characterizing tank 241-C-103. Phases 3 and 4 are tank characterization phases.

Early development work, now complete, involved the collection of vapor samples from tank 241-C-103 for preliminary analysis and the working out of laboratory and logistical problems. These samples were not expected to be representative of the headspace, and the data obtained has been viewed as preliminary. The samples were taken to test the logistics of obtaining and transporting samples, as well as to provide samples for method selection at the analytical laboratories supporting the Vapor Program.

The goal of Phase 1, now complete, was to develop the ability to collect samples from the tank headspace for the purpose of comparing different sampling and analytical methods. The Phase 1 samples will be as representative of the headspace as possible, but analytical methods are not expected to be sufficiently refined to provide definitive, quantitative results. To determine the adequacy of the methods based on analytical parameters (i.e., limit of detection, precision, accuracy, and number of analytes), Phase 1 data has been reviewed by an external committee, VCC, and a panel of expert analytical chemists from national laboratories. The committee recommended a preferred sampling and analysis methodology (Story 1994).

The Phase 1 data was reviewed by the TRP to determine the analytes of toxicological concern (Goheen 1994). Methods selected from the results of Phase 1 will be extended to include these analytes in order to adequately characterize tank 241-C-103 in Phase 2. Phase 2 will involve repeated sampling of tank 241-C-103 to examine tank headspace composition fluctuations, as well as the reproducibility of sampling and analysis procedures. The VSS, which will be used to perform Phase 2 sampling, uses a versatile, valved manifold with precise pressure, temperature, and flow control to collect samples. The VSS has limited analytical abilities, as well.

Phase 3 of the Vapor Program will address 16 of 36 suspect tanks identified at the Hanford Site in FY 94. The extent to which each of the tanks will be characterized may vary as dictated by the data quality objective (DQO) process.

Figure 3-1. Tank Headspace Characterization Logic.

All vapor characterization objectives beyond those of Phase 3 (FY 94) are at the present time included in Phase 4. In Phase 4 (FY 95), an additional 19 waste tanks, for a total of 36 waste tanks, will be characterized. All other tanks will be screened via the WHC/ESQ area and source monitoring program for the presence of noxious vapors. Currently, Vapor Program characterization efforts concentrate on 36 high-priority suspect waste tanks. Suspect tanks are those waste tanks that have a history of vapor exposure or are on the Ferrocyanide, Organic, or High Heat Watch Lists.

Waste tanks designated at this time for vapor characterization include the 20 Ferrocyanide Watch List tanks, the 9 tanks on the Organic Salts Watch List (one of which is also on the Ferrocyanide Watch List), the remaining 7 non-organic Salts or Ferrocyanide Watch List large waste tanks in 241-C tank farm; and tank 241-BX-104, which has been associated with fugitive vapor emissions in the past. Table 3-1 lists the 36 suspect tanks of the Vapor Program. In addition to these 36 waste tanks, the Vapor Program will collect headspace vapor samples from other waste tanks when there are cost-effective sampling opportunities.

3.5 QUALITY ASSURANCE

Quality Assurance (QA) is an integral part of the Vapor Program. It provides independent oversight at planning, implementation, and completion stages to ensure that stated objectives are met. The QA process provides: (1) methodology review; (2) statistical analyses of data collection, analysis, and interpretation; and (3) data validation and records management.

The DQO process is used to verify and validate the data needed to meet the overall Vapor Program objectives. Because of differing data sets, separate DQO's were conducted on flammability, toxicity, and health and safety.

The Vapor Program will participate in organic liquid, FeCN and rotary-made core drilling DQOs. At the Hanford Site, the DOE has the primary responsibility to ensure that performed activities are handled in an efficient and cost-effective manner. To control the quality of activities, DOE has imposed DOE Order 5700.6C (DOE 1991), which is implemented by the U.S. Department of Energy, Richland Field Office (DOE-RL). This order requires the selective and judicious application of requirements from the national consensus standard *ASME NQA-1-1989, Quality Assurance Requirements for Nuclear Facilities* (ASME 1989). Projects within the Vapor Program that impact the environment will meet quality program requirements imposed by the Tri-Party Agreement (TPA). This agreement (Ecology et al. 1994) specifies that all parties shall use procedures for QA and quality control in accordance with EPA methods. Guidance is provided in EPA QAMS 005/80, *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans* (EPA 1983), and EPA/540/G-87/003, *Data Quality Objectives for Remedial Response Activities* (EPA 1987).

Table 3-1. Vapor Program Suspect Tanks.

TANK	CONCERN	PHASE
B-103	Organic	4
BX-102	FeCN*	4
BX-104	Vapor History	3
BX-106	FeCN	4
BY-103	FeCN	4
BY-104	FeCN and Vapor History	3
BY-105	FeCN	3
BY-106	FeCN	3
BY-107	FeCN	4
BY-108	FeCN	4
BY-110	FeCN	4
BY-111	FeCN	4
BY-112	FeCN	4
C-101	Vapor History	3
C-102	Vapor History	3
C-103	Organic and Vapor History	1 and 2
C-104	Vapor History	3
C-105	Vapor History	3
C-106	High-Heat and Vapor History	3
C-107	Vapor History	3
C-108	FeCN and Vapor History	3
C-109	FeCN and Vapor History	3
C-110	Vapor History	3
C-111	FeCN and Vapor History	3
C-112	FeCN and Vapor History	3
S-102	Organic	4
SX-106	Organic	4
T-107	FeCN	4
TX-105	Organic	4
TX-118	Organic and FeCN	4
TY-101	FeCN	4
TY-103	FeCN	4
TY-104	FeCN	4
U-106	Organic	3
U-107	Organic	4
U-111	Organic	3

*Ferrocyanide $[\text{Fe}(\text{CN})_6]^{+}$

WHC directs compliance with DOE quality program requirements in WHC-CM-4-2, *Quality Assurance*. This imposes the criteria of ASME NQA-1-1989, *Quality Assurance Requirements for Nuclear Facilities* (ASME 1989), on all quality-affecting activities performed by WHC personnel. The EPA quality requirements are specified in the existing quality programs to ensure overall compliance with the TPA.

Quality Assurance provides independent review and oversight to the Vapor Program during all stages of development. This activity provides input regarding requirements and whether or not they are being met.

This program is responsive to WHC-CM-4-2, the WHC Quality Assurance Manual. A Quality Assurance Project Plan has been written to address characterization of tank C-103, and will be revised to extend coverage to all other sampling events. Audits, surveillances and assessments will be established in accordance with the QA requirements to ensure that activities are completed as defined.

TWRS Programs Quality Assurance will be the primary QA point of contact with the Vapor Program, and will interface with the other quality assurance groups to assure adequate oversight.

DQOs have been developed using guidance provided in EPA/540/G-87/003, *Data Quality Objectives for Remedial Response Activities* (EPA 1987). The DQOs used in this program are outlined in Task 1.2. As the program continues, more DQOs may be developed using the same guidance.

3.6 PROGRAM PEER REVIEW STRATEGY

3.6.1 Vapor Field Sampling Team

The Vapor Sample Team consists of WHC operations personnel, scientists, engineers, and schedulers. This group meets to discuss problems, sampling events, and scheduling matters.

3.6.2 Vapor Conference Committee

The Vapor Conference Committee consists of gas sampling and analysis experts from other DOE sites, Oak Ridge National Laboratories (ORNL), Sandia National Laboratories (SNL), Ames Laboratories, Oregon Graduate Institute (OGI), University of California, Berkeley, University of Washington, and Northwest Instrument Systems, Inc. (NISI).

3.6.3 Vapor Technical Team

The Vapor Technical Team is a team of scientists and engineers from WHC, PNL, and NISI that meets weekly to resolve technical problems and advise the Vapor Program.

3.6.4 Tank Vapor Task Team

The Tank Vapor Task Team consists of industrial hygienists, chemists, chemical engineers, and toxicologists from WHC, PNL, ICF/Kaiser Engineers Hanford, NISI, and DOE.

3.6.5 Tank Advisory Panel, Subpanel on Worker Health and Safety

The Tank Advisory Panel (TAP), and in particular the Subpanel for Worker Health and Safety, is a DOE panel of nationally recognized scientists from Idaho National Engineering Laboratory, Science Applications International Corporation, Harvard University, Los Alamos National Laboratory, and DOE. This group serves as an oversight panel, making its recommendations to DOE.

3.6.6 Waste Management External Advisory Committee

The Waste Management External Advisory Committee is a group of nationally recognized experts contracted by WHC to assist in the evaluation of various issues. Members are available for limited support of the Vapor Program on an as-needed basis.

3.6.7 Toxicology Review Panel

The TRP is a group of toxicologists and scientists in related fields from PNL and Hanford Environmental Health Foundation (HEHF). The purpose of this group is to review tank vapor characterization data and make recommendations to WHC on the health risks indicated by the data.

4.0 TANK VAPOR PROGRAM STRATEGY, LOGIC AND DOCUMENTATION

The transition from development and testing (Phases 1 and 2) to practical and routine implementation of vapor characterization methods (Phases 3 and 4) are discussed in this section. Other planned activities that support the Vapor Program goals are described in Section 5.0. These include the systematic study of vapor release mechanisms, current plans for ensuring worker safety, an industrial hygiene monitoring program to evaluate vapor hazards to workers, and current treatment/remediation activities.

4.1 SITE-WIDE TANK VAPOR CHARACTERIZATION

Characterization of the waste tank vapors is a key element of the Vapor Program's strategy to resolve the health and safety issues associated with noxious vapors in the tank farms. Once the adequacy of selected characterization methods has been established by successful completion of Phases 1 and 2, these methods will be applied to study the remaining 35 suspect waste tanks at the Hanford Site. This effort has been divided into Phases 3 (FY 94) and 4 (FY 95).

One of the goals of Phase 3 will be to characterize, to an appropriate extent, the noxious vapors in 16 suspect waste tanks. In Phase 3, the Vapor Program will advance both its technical and procedural bases, with the goal of converting what is now an arduous and novel sampling process into an established and routine procedure.

Characterization of vapors in the remaining 19 suspect waste tanks will be performed in Phase 4. Though each waste tank has unique features, the tank-by-tank vapor characterization should not involve major developmental efforts in Phase 4. Exhaustive characterization is not a goal in and of itself, and the extent to which sampling and analysis must be performed in any given tank to meet Vapor Program objectives cannot be determined *a priori*. It is anticipated that many waste tanks will have little or no vapors of concern, and that this can be ascertained from relatively inexpensive preliminary sampling.

Two general methods will be used to collect waste tank air samples. The first method will involve the use of heated sampling probes inserted into the tanks, a heated transfer line, and a heated sampling manifold (VSS). This system has been designed to transfer representative air samples from the headspace to a convenient sampling location, a strategy particularly well suited for taking a broad array of samples. The second method of waste tank air sampling will rely on a small number of sample collectors, some of which will be inserted directly into the tank headspace. This approach will be used for early screening of tanks, and to measure the concentrations of a limited number of specific vapors. While it has limitations, this second sampling method has an advantage in that it can be conducted as an adjunct of other intrusive waste tank activities, and hence could be very cost effective. The logic leading to resolution of the tank vapor issue is presented in Figure 4-1. Discussion of the specific tasks identified in the logic diagrams follows each of the figures. These logic diagrams show the

Figure 4-1. Overview of Waste Tank Safety Issue Resolution Logic. (1 of 7)

Figure 4-1. Overview of Waste Tank Safety Issue Resolution Logic. (2 of 7)

Figure 4-1. Overview of Waste Tank Safety Issue Resolution Logic. (3 of 7)

Figure 4-1. Overview of Waste Tank Safety Issue Resolution Logic. (4 of 7)

Figure 4-1. Overview of Waste Tank Safety Issue Resolution Logic. (5 of 7)

Figure 4-1. Overview of Waste Tank Safety Issue Resolution Logic. (6 of 7)

Figure 4-1. Overview of Waste Tank Safety Issue Resolution Logic. (7 of 7)

flow of work and major task relationships used to arrive at the zero option or to evoke mitigation or remediation of the source of the vapors. More specific logic diagrams are used throughout the program plan to clarify technical or decision tree processes and for clarity.

TASK 1.0 - EVALUATE AND DEFINE THE PROBLEM

Task 1.1 - Review Historical Incidents

Task 1.1.1 - Vapor Exposure History

Twenty-two vapor exposure events involving 39 people at the Hanford Site have occurred between July 1987 and April 1994. All the vapor exposures involved first aid medical consultation, and two cases resulted in significant amounts of lost time to workers. 10 of these vapor exposure events, involving 18 people, were associated with the 241-C tank farm. These events are described in the following summaries:

- **July 1987**--An exposure to three individuals working on a portable exhauster occurred at tank 241-C-103. This exposure resulted in significant lost time to two of the workers.
- **July 1987**--A vapor exposure incident was reported involving two operators moving a filter housing from tank 241-C-106 to tank 241-C-103.
- **January 1989**--An operator involved in routine duties in the 241-C tank farm reported a vapor exposure incident.
- **August 1989**--A technician involved in a routine surveillance in the 241-C tank farm reported a vapor exposure incident. Post-incident analysis indicated tank 241-C-103 as the source of the vapor.
- **March 1991**--A technician near a pit for tank 241-C-103 reported an vapor exposure incident.
- **September 1991**--Three workers performing maintenance activities on tank 241-C-103's activated charcoal filters experienced a vapor exposure incident.
- **September 1991**--A vapor exposure incident occurred involving one construction worker who was excavating in the 241-C tank farm.
- **September 1991**--A vapor exposure incident occurred involving two insulators installing a greenhouse in the 241-C tank farm.

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- **September 1991**--A vapor exposure incident occurred involving two construction personnel working outside the 241-C tank farm gates.
 - **May 1992**--Two Health Physics technicians were affected by vapor while working at the 241-C vault, which was downwind of tank 241-C-103.

Tank Farm Operations management's response to these events included: (1) initiation of forced ventilation of tank headspaces; (2) provisions for respiratory protection for workers within the tank farm and within specified boundaries; (3) initiation of area IH monitoring; and (4) installation of filtration devices on tank vent lines. The activated carbon filters on tank 241-C-103, for example, were installed in December 1989, with the rationale that this tank was the prime source of noxious vapors and that ammonia was the major contributor. Many corrective actions were assigned to organizations that had neither the budget nor the expertise to complete the actions, and progress in resolving the vapor issues has been limited by other tank farm issues with higher priorities (e.g., the episodic gas releases in 241-SY-101 and the ferrocyanide issues).

The sporadic timing and varied locations of vapor exposure incidents have meant that these occurrences have historically been treated as isolated incidents. A January 28, 1992 battery acid fume exposure incident, however, prompted a complete reassessment of management responses to these types of potential worker exposure incidents in general. Although this vapor exposure incident was not linked to a waste tank fugitive vapor emission, it highlighted the need for a comprehensive, dedicated program to resolve the vapor exposure issues.

The use of supplied air for an indefinite period to maintain worker safety in certain tank farms is unsatisfactory. However, until the noxious vapors are identified and measured, and a more appropriate solution to the exposure problem is found, conservative safety measures will remain in effect in areas of tank farms with the highest exposure potential*.

One of the key elements required to minimize worker exposure to noxious vapors is the positive identification of the noxious vapors in the source. This can only be done by a reasonably complete qualitative and quantitative characterization of the waste tank vapors, both organic and inorganic species.

No comprehensive site-specific health and safety plan** existed in January 1992 dealing with and minimizing vapor-related IH concerns. An active IH monitoring program was clearly needed to help identify problems before they compromised workers' health;

*Workers within buffer zones around tanks 241-C-102 and 241-C-103 are currently required to be on supplied air because of the unknown risk of noxious vapor exposure.

**The Tank Farm Health and Safety Plan, WHC-SD-WM-HSP-002 (1993), has been implemented in the tank farm complex.

procedures were also needed for dealing with vapor-related incidents if and when they occurred. For the IH air monitoring strategy to be effective, source term vapor information from the in-tank characterization effort is essential to correctly target worker exposure assessments.

Because of a trend identified in the vapor exposure incidents, tank 241-C-103 is considered the "worst case" tank and is the near-term focal point of this program plan. Sampling and analytical methodology development accomplished in the pilot characterization of tank 241-C-103 will be used as the basis to characterize the remainder of the Hanford Site waste tanks. The comprehensive tank farm site-specific health and safety plan is the cornerstone of the WHC IH program.

Task 1.1.2 - Flammability of Organic Vapors and Aerosol in Tank 241-C-103

The highest concentration of flammable organic vapors in any waste tank is thought to exist in tank 241-C-103. This tank is known to contain a layer of semi-volatile organic liquid floating on an aqueous waste liquid. The organic liquid is thought to have come from the plutonium-uranium extraction (PUREX) process. It was added to tank 241-C-102 accidentally, and transferred to tank 241-C-103 in 1975. Its principle constituents, based on its origin in the PUREX process and a recent liquid assay (Pool and Bean, 1994), are TBP and NPH.

While the concentration of possible vapor above the organic liquid in tank 241-C-103 is well below its lower flammability level (LFL) (Van Tuyl 1983), the presence of an organic aerosol in the headspace of tank 241-C-103 could increase the headspace fuel concentration substantially. To address this concern, the Vapor Program commissioned and released *An Engineering Assessment of the Aerosol and Vapor Flammability in 241-C-103* (Huckaby and Estey 1992). In this assessment, a conservative estimate of the flammable constituents of the headspace (organic vapors and aerosol) places concentrations at less than 20% of the LFL. Chester Grelecki of Hazards Research Corporation (which is on contract to WHC via the Waste Management External Advisory Committee) reviewed the assessment and concurred that the methods and assumptions made in evaluating the tank headspace flammability were indeed conservative.

The historical presence of an aerosol in tank 241-C-103, and some other important aspects of the tank headspace, can be understood by considering the temperature differences between the liquid surface and the tank dome. Near the liquid surface, which is about 42° C (107 °F), the air is warmed and nearly saturated with the vapor of the liquid. This warm, moist air rises within the headspace, being displaced by cool, dense air from near the concrete dome of the tank. As the warm moist air mixes with the cooler air, it is cooled below its dew point, and condensation of the vapor results in an aerosol. The convection,

which results from the warm air being displaced by the cooler dome air, mixes the headspace vertically, resulting in minimal stratification of the headspace; temperature and the total concentration of fuel (vapor plus aerosol) should not differ significantly with height in the tank.

Flammability of a fuel aerosol depends on the size of the individual aerosol droplets. When an organic liquid is burned, it first must be vaporized because it is the vapor that burns with the oxygen in air. Small fuel aerosol droplets, with diameters below about 1 μm , can evaporate completely as a flame front moves past them, and contribute their total fuel to flame propagation. Fuel droplets with diameters between about 1 μm and 10 μm may not completely evaporate as a flame front passes, and contribute only part of their fuel to flame propagation. Fuel droplets having diameters greater than 10 μm do not evaporate significantly while a flame front passes; consequently, they do not contribute significantly to flame propagation. Thus, it is conservative to sample the aerosol and vapor and assume the entire fuel mass collected to be in the vapor phase.

The possibility that a flammable condition exists in the headspace of tank 241-C-103 must be addressed. Standard tank farm procedure has required that a calibrated combustible gas meter (CGM) be used to evaluate the headspace of tank 241-C-103 prior to vapor sampling or intrusive work, and that work shall be stopped if the measured concentration of flammable gases and vapors is above 20%* of the LFL. Unfortunately, the CGMs are relatively insensitive to the major flammable constituent, NPH, of tank 241-C-103, and cannot properly sample, measure, and account for this fuel constituent. As a result, the total flammability (both aerosol and vapor) of the tank headspace must be measured by an alternative method. (See Task 1.3.4).

Task 1.1.3 - Waste Tank 241-C-103

Current understanding of the Hanford Site waste tanks indicates that, of the SSTs, tank 241-C-103 has the greatest potential to be flammable. This tank also has been involved in the largest number of vapor exposure incidents. Tank 241-C-103 is a 1.9-ML (530-kgal) SST constructed in 1943-1944. It is the third tank in a 3-tank cascade series, and is connected via a 7.6-cm (3-in.) pipe to tank 241-C-102; tank 241-C-102 is similarly connected to 241-C-101.

*Quoting Section 2-6.2 of NFPA 497A (NFPA 1993f), "Adequate ventilation is defined by NFPA 30, Flammable and Combustible Liquids Code, as that which is sufficient to prevent accumulation of significant quantities of vapor-air mixtures in concentrations over 25% of the lower flammable limit." WHC has chosen a more conservative point, or 20% of the LFL, as the action level for waste tank headspace.

Tank 241-C-103, like the majority of SSTs, is not actively ventilated. Barometric and other pressure differences between the tank and the atmosphere are relieved by passive ventilation. Air exhausted by the tank passes through: (1) a HEPA filter intended to remove radioactive particulates; and (2) an activated charcoal filter designed to remove organic vapors and ammonia. Currently, the available HEPA breathing filters on tanks 241-C-101 and 241-C-102 are valved off, so that these tanks breathe through the HEPA and charcoal filter of tank 241-C-103. An important consideration is that the tank headspace is, at least part of the time, at a higher pressure than the atmosphere, so that despite the available venting, cracks or other small openings in the tank could potentially leak vapors directly to the environment.

Tank 241-C-103 contains about 757 kL (200 kgal) of waste, of which about 522 kL (138 kgal) is thought to be supernatant liquids; the remaining 235 kL (62 kgal) is sludge. The waste is approximately 173 cm (68 in.) deep, with the upper 127 cm (50 in.) being supernate. The sole thermocouple tree in the tank is about .91 m (3 ft) from the tank wall and has 4 thermocouples, located at .51 m, 0.61 m, 1.22 m, and 4.5 m (0.2 in., 2 ft, 4 ft, and 14 ft 10 in.) from the tank bottom. On March 14, 1994, the temperatures were observed to be 46.7, 46.1, 40.6, and 36.7 °C (116, 115, 105, and 98 °F), respectively. The temperatures from these thermocouples are observed to vary with the seasons within a range of about 5 °C (9 °F). The highest temperatures have been observed in October; the lowest in April. The third thermocouple is about 45.7 cm (18 in.) below the waste surface, while the fourth thermocouple is about 2.8 m (9 ft 4 in.) above the waste surface.

Several important characteristics of tank 241-C-103, based on physical measurements and chemical analyses of the supernate (Pool and Bean 1994) are:

- The ratio of nitrite to nitrate ion concentrations in the aqueous supernate is about 9.4 to 1 (much higher than in most other tanks).
- The aqueous supernate radionuclide concentration is relatively low.
- The aqueous supernate pH is approximately 10.0 (which is lower than most other tanks).
- A layer of organic liquid 3.8 cm to 5 cm (1.5 to 2 in.) deep, thought to have originated in the PUREX process, is floating on the aqueous supernate.
- The organic liquid layer is composed principally of TBP and NPH.

A summary of available data on tank 241-C-103 has been given by Postma et al. (1994).

TASK 1.2 - DEVELOP DATA QUALITY OBJECTIVES AND DECISION RULES

DQOs for generic tank vapor sampling were developed in a series of four facilitated meetings and one stakeholder review session, using the most recent seven-step EPA DQO guidelines. These meetings elicited DQOs for two major vapor problem areas: flammability and toxicity. More details regarding the rationale for each of the DQO planning outputs are contained in WHC-SD-WM-DQO-002, *Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution* (Osborne et al. 1994b). A specific DQO, WHC-EP-0774 (Osborne et al. 1994a), was prepared for tank 241-C-103 because of its unique characteristics.

Task 1.2.1 - Problem Statement

Two problems were: (1) potential flammability of gases and vapors in waste storage tanks; and (2) potential worker health and safety hazards associated with the toxicity of constituents in any fugitive vapor emissions from the waste tanks. Previous work reports the presence of a fog in some tanks, and the fuel content of tank gases and vapors may be too high to permit work in those tanks. Workers have made numerous reports of adverse health effects associated with vapor exposures in and around tank farms. Confirmed symptoms include headaches, burning sensations in nose and throat, nausea, and impaired pulmonary function.

Data are needed to identify and quantify constituents of the tank headspaces to address potential vapor toxicity. If any compounds of toxicological interest are identified in the tank headspaces, industrial hygienists can use this information to assess "worst-case" worker exposure levels and focus the industrial hygiene monitoring strategy on these target compounds. Final recommendations on the required PPE level will be based on the worker breathing zone levels of these chemicals. The ultimate goal is to provide a safe and healthful workplace in the tank farms complex.

Resolution of these problems involves a sequence of sampling events. The first sampling event assesses flammability of the volatile organic vapor, ammonia, methane, and other flammable gases present in the tank headspace. If the flammability assessment results are acceptable, then special vapor sampling equipment will be installed in the tank. This equipment will be used in subsequent sampling events to: (1) establish concentrations of all flammable headspace constituents; (2) identify compounds of toxicological concern; and (3) quantify compounds of toxicological concern.

Task 1.2.2 - Decision Statements/Inputs to the Decision

A. Flammability Decision

If the total fuel content of the headspace is $\geq 20\%$ * of the LFL, then according to the tank farm Operating Safety Document (OSD), work must stop until further authorization is given by management.

B. Toxicity Decision

If any compounds with toxicological properties exceed their recommended levels inside the tank headspace, then advise Health and Safety. Guidelines are:

- 10% of the appropriate CES concentration for known or suspected human carcinogens, teratogens and mutagens
- 50% of the appropriate CES concentration for non-carcinogens, non-teratogens and non-mutagens, or simple irritants
- Identification and quantification of flammable constituents in the headspace
- Temperature of the headspace
- Identification and quantification of compounds of toxicological importance
- Understanding of the toxicological effects of these compounds and the CES for each constituent of concern.

Task 1.2.3 - Boundaries of the Study

The spatial boundaries of the vapor and gas sampling events are defined by the waste surface, walls and dome of the waste tank itself. Sampling events will be scheduled to address diurnal, seasonal, and long-term changes in the vapor and gas concentrations.

*Quoting Section 2-6.2 of NFPA 497A (NFPA 1993f), "Adequate ventilation is defined by NFPA 30, Flammable and Combustible Liquids Code, as that which is sufficient to prevent accumulation of significant quantities of vapor-air mixtures in concentrations over 25% of the lower flammable limit." WHC has chosen a more conservative point, or 20% of the LFL, as the action level for waste tank headspace.

Task 1.2.4 - Toxicity Decision Rule

The DQO team established decision rules organizing potentially toxic substances by type to include carcinogens, teratogens and mutagens, systemic toxins, and irritants. The toxicity decision rules were specified as follows:

- If the average concentration of any confirmed or suspected human carcinogen, teratogen, or mutagen in a tank headspace is greater than one-tenth of its CES, then advise the IH group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.
- If the average concentration of any systemic toxin in a tank headspace is greater than one-half its CES, then advise the IH group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.
- If the average concentration of any irritants in a tank headspace is greater than one-half of its CES, then advise the IH group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.

Task 1.2.5 - Flammability Decision Rule

If the total fuel content of the headspace is $\geq 20\%$ * of the LFL, then according to the tank farm Operating Safety Document (OSD), work must stop until further authorization is given by management.

Task 1.2.6 - Limits on Decision Errors

A. Flammability Decision Errors

One type of decision error would occur if data incorrectly indicate $LFL_{MIX} \geq 20\%$

A second kind of decision error would occur if data incorrectly indicate $LFL_{MIX} < 20\%$.

*Quoting Section 2-6.2 of NFPA 497A, "Adequate ventilation is defined by NFPA 30, Flammable and Combustible Liquids Code, as that which is sufficient to prevent accumulation of significant quantities of vapor-air mixtures in concentrations over 25% of the lower flammable limit." WHC has chosen a more conservative point, or 20% of the LFL, as the action level for waste tank headspace.

B. Toxicity Decision Errors

One type of decision error would occur if data incorrectly indicate that the prescribed toxicity limits have been exceeded, when in fact they haven't.

A second type of decision error would occur if data incorrectly indicate that the prescribed toxicity limits have not been exceeded, when in fact they have.

The relative consequence of the second type of decision error (failure to find a true problem) was determined to be roughly 2.5 times greater than the other type of decision error.

Task 1.2.7 - Sampling and Analysis Design

The WHC strategy to resolve the flammability and toxicity issues was approved by DOE reviewers prior to initiation of this DQO (Christensen 1993, Gerton 1992, O'Dell 1992). The DQO process was consequently limited by constraints imposed by these designs. Therefore, Step 7 addresses the expected performance of the flammability assessment sampling and the proposed sampling strategy for determining headspace vapor and gas toxicity.

TASK 1.3 - SAMPLE AND CHARACTERIZE TANK VAPORS

This section of the program plan describes the applied methodology and technology implemented by the Vapor Program to resolve vapor issues associated with tank 241-C-103. The selection of equipment and methods for qualitative and quantitative characterization of the tank 241-C-103 headspace is discussed. Included in this section is an item expected to be unique to tank 241-C-103: resolution of the flammable vapors and aerosol issue.

Task 1.3.1 - Develop Analytical Methods

Task 1.3.1.1 - Introduction

The Vapor Program sampling and analysis strategy must address the safety and industrial hygiene issues related to waste tank vapors. To address these issues, the Vapor Program will identify and quantify the vapors present in the tank headspaces as completely as is reasonably possible. A phased approach will be used to determine the most effective and expedient methods for tank vapor characterization. Four phases have been defined in the site-wide program, with each phase supplying the specific information needed for any decisions affecting the subsequent phase.

In the first two phases, the Vapor Program will develop and test the technologies and methodologies necessary to characterize the vapors in the tank 241-C-103 headspace. Figure 4-2 illustrates the logic sequence for Phases 1 and 2. Phases 3 and 4 of the Vapor Program will supplement, adapt, and apply the acquired methods to resolve all other vapor issues associated with the Hanford Site waste tanks. Specifically, the goal of Phase 1 was to develop the equipment and expertise to collect representative samples from the headspace of tank 241-C-103. Phase 2 will begin when the capability to characterize the vapors in tank 241-C-103 is functional.

With the reasonably complete characterization of a tank headspace, evaluation of the health and safety hazards associated with the vapors and vapor releases from tank 241-C-103 can be evaluated using a variety of accepted guidelines. Institutional and regulatory agencies have published guidelines for evaluating the hazards associated with worker exposure to vapors. For example, the threshold limit value, 8-hour time weighted average, and LFL of vapors can be used to evaluate toxicological and safety hazards.

Once tank 241-C-103 has been characterized, the fundamental sampling and analytical methodologies necessary for continued tank farm characterization and monitoring will be available at the Hanford Site. The characterization of 35 suspect waste tanks will take place by the end of FY-95. All other tanks will be evaluated via *in situ* vapor sampling by the TWRS Characterization group from FY-96 through FY-97. This pilot study of tank 241-C-103 will develop the technological, logistical, and managerial expertise needed for long-term characterization of the remaining waste tanks.

Task 1.3.1.2 - Sampling

Previous vapor characterization studies of tank 241-C-103 did not adequately define the tank vapor composition or resolve the vapor issues. This was a result of the incomplete development of the sample collection and sample handling techniques. There are, in fact, no validated organic chemical sampling methods that cover all compounds on the extensive list of analytes found to date in tank 241-C-103. Furthermore, the relatively high vapor concentrations expected in tank 241-C-103 limit the application of validated sampling techniques. Consequently, the Vapor Program will modify, as necessary, currently accepted analytical sampling methods to accomplish the intended vapor characterization. The list of candidate sampling methods, design of the sampling apparatus, selection of the sampling method, chemometrics, and sample method verification will be reviewed by the Vapor Conference Committee through a panel of external experts in analytical methods.

Figure 4-2. Vapor Program Phase 1 and 2 Logic.

The three sample techniques suggested by the Vapor Conference Committee to be evaluated are as follows:

- **Sorbent traps**--These collectors are typically small, pencil-sized stainless steel or glass tubes packed with a collection (sorbent) medium. A pump is used to pull an air sample through the tube, and specific analytes in the air are adsorbed by the sorbent packing. The sample is then taken to a laboratory for desorption of the analytes and subsequent analysis by a gas chromatograph with a mass spectrometer detector (GC/MS), or by a gas chromatograph with a flame ionization detector (GC/FID). The term "multi-sorbent tube" refers to a sorbent tube specifically designed with more than one kind of sorbent to collect a wider range of chemical compounds.
- **SUMMA® canisters**--These are 6-L stainless steel containers that are evacuated. Opening a valve fills the canister rapidly with a grab sample of vapor. Alternatively, an orifice can be used to limit the inflow of vapor so that an integrated sample can be taken over a predetermined period of time.
- **Direct sampling GC/MS**--This technique uses a pump to pull a vapor sample directly into a GC/MS at the sampling location. This option basically bypasses the need to collect the sample by other means (i.e., sorbent traps or SUMMA® canisters) and transport them to the laboratory.

Because of time, cost, and technical adequacy, only two sampling techniques will be used to characterize tank 241-C-103: the sorbent tube and SUMMA® canister sampling techniques. Direct sampling GC/MS techniques are being developed for a limited list of analytes; however, these will not be adequately developed for the analytical characterization in Phases 1 and 2.

In Phase 1, samples were collected from the tank 241-C-103 headspace using a temperature, pressure, and flow controlled sampling manifold. This manifold will be capable of sampling at three different levels of the headspace of tank 241-C-103, with SUMMA® canisters and sorbent tubes. Only 1 level was used in Phase 1. In Phase 2, this manifold and the sampling method will be applied in a series of sampling events at three levels to evaluate the performance of the system and characterize the tank 241-C-103 headspace over a period of time. Multi-level characterization will address the issue of vapor stratification in the tank headspace. While this information is important, it is not a critical path for tank 241-C-103 characterization or safety issue resolution.

*SUMMA is a registered trademark of Moleetrics, Inc., Cleveland, Ohio.

Task 1.3.2 - Validation of Analytical Methods

The lack of an accepted procedure like EPA toxic organic analysis method (EPA TO) 14, which has been validated for the chemicals of interest found in the head space of the Hanford waste tanks, will require a limited "validation-like" regime that is acceptable to the analytical community. A procedure involving a standard addition spike has been recommended by the Vapor Conference Committee (VCC) for this application. A schematic of the validation process logic is given in Figure 4-3. This procedure is commonly used when repeated analysis is needed for a changing matrix.

In the standard addition spike method, known amounts (spikes) of the analytes of interest are added to a real sample, and the analytical responses to these added amounts are compared to those expected. This validation method will be performed for all analytes of interest identified by a panel of toxicologists. A standard gas mixture of the chosen analytes will be prepared that is traceable to a known standard. This gas mixture will have analyte vapor concentrations 3 to 4 times greater than those expected in the tank sample. Analysis of this mixture will yield a response factor for each chemical in the standard. The standard mixture will be analyzed separately, and a response factor tabulated. The two response factors will be compared for significant deviations.

As a part of the validation strategy, the standard gas mixture, tank sample, and spiked sample will be analyzed periodically to determine any holding time effects. Conclusions from this study will then be incorporated into the analytical methodology. This approach to validation of the sampling and analytical methods will be required for each tank's unique chemical matrix. This "validation-like" effort is not an attempt to expand the list of analytes associated with the EPA TO-14 protocol.

Task 1.3.4 - Resolution of Headspace Flammability

The Vapor Program has collected and analyzed samples to address the potential flammability of the tank 241-C-103 headspace. Results to date indicate the fuel content of the headspace is well below its LFL. Samples collected directly from riser ports during November 1993 were used to estimate concentrations of hydrogen, methane, and ammonia. *In situ* sampling performed in December 1993 established the concentrations of the NPH, and that no visible aerosol was present during inspections of the headspace on different days. Samples to address headspace flammability were also collected in January 1994 with the VSS. Results affecting the flammability assessment have been generally consistent; however, future sampling is planned to address the seasonal variation of headspace constituents. Detailed information on the sampling events, analytical results, and a summary of available information on the headspace flammability are given in Huckaby (1994) and Postma et al. (1994).

Figure 4-3. Validation Process Logic.

Task 1.3.5 - Perform Toxicity Sampling and Analysis

The sampling methods chosen for Phases 1 and 2 above rely on laboratory analysis by GC/MS. The ability of GC/MS to separate and quantitate components of a mixture of this sort is well recognized by the analytical chemistry community.

The currently accepted analytical methods (e.g., EPA TO-14) for organic vapor analysis are validated only for a specific list of analytes. These methods are applicable to low vapor concentrations, as might be found in ambient air near tank 241-C-103. However, it is known from previous work that many compounds in tank 241-C-103 are not on the list of validated compounds for these methods, and some of the vapor concentrations in the headspace are too high to satisfy validation criteria. Of the three methods considered by the Vapor Conference Committee, two accepted laboratory methods were selected as being adaptable to the vapor characterization needs of tank 241-C-103. These are sorbent tube sampling followed by GC/MS, and SUMMA® canister sampling followed by GC/MS. The GC/MS procedure is different for these two sample collection methods.

Samples collected will be sent to external national laboratories (e.g., PNL, ORNL, SNL) qualified in the selected analytical methods. A sufficient number of samples, as dictated by the sample and analysis plan, will be taken by sorbent and SUMMA® methods and analyzed to allow estimation of precision on a statistical basis. Selection by the VCC of the method to be used will be based on precision, list of analytes detected, and estimated limits of detection.

Phase 1 generated data needed to select the best sampling and analysis methods. The data obtained in Phase 1 will only be of sufficient quality to identify the list of compounds present; the analytical results of Phase 1 were not expected to be of sufficient quality to quantitatively characterize the vapor phase.

A list of 160 analytes found by all methods in Phase 1 was compiled and submitted to a panel of toxicologists (TRP) for determination of the analytes of importance. The panel returned an interim report titled *Interim Report of the Toxicology Review Panel and Selection of Analytes from Tank 241-C-103 for Additional Information* (Goheen 1994) on April 13, 1994 identifying 19 analytes of toxicological interest. Those analytes not already validated quantitatively for the selected methods will be validated in Phase 2. The Quality Assurance Project Plan will identify sampling and analytical quality criteria.

The analysis reports and data from each technique have been reviewed by the VCC, which has provided recommendations for method selection. Selected methods will be optimized in Phase 2, and validation of analytes will be performed. Also in Phase 2, the requirements for the analysis of inorganic vapors will be determined. Phase 2 will terminate with the definitive characterization of the vapor constituents in tank 241-C-103. Phase 2 will provide valuable information to focus the WHC/ESQ air monitoring campaign, and will provide sufficient characterization of the tank vapors (hazardous, flammable, and permanent gases) to permit the engineering of a remediation system for tank 241-C-103 if needed.

The need for future waste tank vapor characterization can best be met and will be least expensive if the sampling and analysis technology is available at the Hanford Site. The Vapor Program is consequently seeking to transfer the necessary technologies from the external national laboratories to the Hanford Site. The analytical approach determined by the VCC to be best for the long term is direct sampling and analysis by GC/MS or GC/FID. This method, which uses a mobile analytical laboratory, is quicker, entails less sample handling, and may be adequate for tank headspaces less complex than tank 241-C-103. This method would also be useful for monitoring tank 241-C-103 once characterization is complete. During Phase 2, the feasibility of direct sampling and GC/FID will be tested in the VSS, with the goal of providing a more cost effective and responsive sampling and analysis methodology for future tank characterization.

Task 1.3.6 - Collect Meteorological Data

A single meteorological station will be used by the Vapor Program in Phase 2 to collect meteorological data in the 241-C tank farm. This solar-powered weather station is currently collecting and storing meteorological data for subsequent transfer to a database. This data will be read to assess weather factors pertinent to work vapor exposure if any should occur in the future. See Section 5.1.2 for more detail on collection and use of microclimate data.

Task 1.3.7 - Enter Vapor Data Into Database

Data generated by the Vapor Program, and all available appropriately related data, will be compiled and stored in a database called VAPORNET. The database will be organized by tanks and will contain all available information pertinent to engineering and policymaking that concerns waste tank vapors. Data of industrial hygiene interest will be shared with the HEHF Industrial Hygiene Database.

Task 1.3.8 - Toxicology Review Panel (TRP) Review Analytes of Interest

A panel of PNL toxicologists will convene to review the matrix validation results and the quantitative data as it is generated. The panelists will make recommendations to the WHC/TWRS Tank Vapor Program Manager concerning potential impacts to worker health and safety. This information will be presented to WHC/ESQ/Waste Tank Safety Support (WTSS) for determination of the appropriate PPE. If PPE is deemed necessary in the short term, longer-term engineering barriers and/or permanent administrative controls will be implemented by WHC/TWRS.

Figure 4-4. Tank Vapor Database System.

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Task 1.3.9 - Validate Analytical Strategy

For the generic tank vapor analysis, the following adaptive analysis strategy will be employed.

If a pre-existing flammable safety concern is relevant, a flammability meter reading and/or an *in situ* sorbent sampling using Occupational Safety and Health Administration (OSHA) versatile samplers and analysis technology as described in *Aerosol and Vapor Characterization of Tank 241-C-103* (PNL-8875/UC-606) (Ligotke et al. 1993) or equivalent will be employed for resolution.

If a pre-existing flammable safety concern is not relevant, a representative sample of the tank headspace will be taken in a manner that has been shown to effectively address any documented concerns and the DQO's for that tank (SUMMA® canisters, sorbent tubes, impingers). Standard, accepted, ambient air analysis methodologies such as chemical class detectors (hydrocarbon, halogen, etc.), gas chromatography, mass spectrometry, ion chromatography or colorimetry will be employed to determine concentrations above 1 part per billion (volume). The analysis will specify by chemical the concentration detected and the confidence of that measurement. Historically-achieved performance can be substituted for non-standard gases. If the list of identified gases contains any analytes that are of concern to the program, e.g., toxicity, those concerns will be judged with respect to the data and a determination made as to the adequacy of the sampling and analysis or whether additional work needs to be done. This may mean the convening of an expert panel, operational controls or other resolution means that are cost effective.

Task 1.3.10 - Advise IH of Monitoring Strategy

Industrial hygiene vapor monitoring is being performed to obtain the data needed to intelligently set the level of protection for tank farm personnel. Ideally, the tank headspace should be fully characterized prior to conducting monitoring to ensure that all chemicals that might be released into the work area are evaluated. However, due to the radioactive nature of the waste, and the fact that each tank may have different vapors present, this characterization will require an extended period to complete. A report from TRP will be sent by the Vapor Program Manager to the WTSS Manager.

TASK 1.4 - CHARACTERIZE WORKERS' BREATHING ZONE

Task 1.4.1 - Develop List of Target Vapors for Air Monitoring Strategy

Two reports will be prepared from the vapor analysis of each waste tank. One is a report on the actual tank vapor analysis; the other is a report by a panel of toxicologists. The tank vapor analysis report will include a description of the sampling effort, identification of the

level of method validation, a summary of the analytical results, and a flammability assessment. The tank vapor analysis report will include as attachments the analytical laboratory report/raw data from all involved laboratories. The TRP will identify (from the analytical results) the vapor categories of toxicological concern for which further method validation is required.

Task 1.4.2.1 - Monitor and Collect Data From Breathing Zone

Task 1.4.2.1 - Personal, Area, and Source Monitoring

The WHC/ESQ/WTSS monitoring plan involves: (1) personal monitoring; (2) area monitoring; and (3) source monitoring. Personal sampling equipment is worn by a worker near the worker's head during normal work activities. Samples are collected from the same air that the worker breathes, and consequently will provide actual worker vapor exposure data. Area monitoring will be conducted with both portable and stationary monitoring equipment, and will be performed to determine the general vapor concentrations in the work area. Source monitoring will be performed to locate the points of vapor release from the waste tanks and to identify specific chemicals present, and will be used in conjunction with the tank vapor characterization to evaluate the potential exposure of workers to high vapor concentrations.

Task 1.4.3 - Enter Data Into Database

Because personal monitors are sampling the same air the employee breathes, they present the best estimate of actual employee exposure. Area monitoring data will be used to supplement these data, when available. Source monitoring will help define "worst case" employee exposure levels, and will identify vapor emission sources for later evaluation and control measures.

TASK 1.5 - APPLY DECISION RULES TO DATA

Task 1.5.1 - Apply Toxicity Rule

Once tank vapor data has been collected for a specific tank farm, an evaluation will be performed by comparing these data to current employee exposure standards. Based on this evaluation, recommendations will be made concerning tank farm control measures, including such elements as respiratory protective equipment, monitoring requirements, engineering controls, and additional monitoring. These recommendations will be given to tank farm management and used to make necessary revisions to existing policies and procedures. As these policies and procedures are updated, informational meetings will be held with tank farm employees to present the results of the sampling efforts and explain any changes prior to

implementation. Sampling and monitoring data will continue to be collected from the farms at a reduced frequency so as to verify that changes are not occurring in a tank farm that would require modification in control levels.

When sampling data indicate that potentially high vapor levels are present in a tank farm, appropriate worker exposure control measures will be implemented. These measures will depend on several factors, including vapor levels, where the vapors were found, and extent of the vapor release. If additional information is needed for a specific tank or farm, continuous area monitors will be used. These monitors will be installed at specific locations to monitor vapor concentrations on a 24-hour basis. The monitors provide a readout of specific vapor concentrations present, and also store the data at specified time intervals. WTSS will use these data to determine vapor release patterns and evaluate maximum release levels.

As TWRS tank vapor headspace characterization efforts continue, data that are collected will be evaluated to determine if additional sampling or monitoring of the employee work area is necessary. If additional sampling or monitoring is required, WTSS will oversee the sampling or monitoring programs, and will provide feedback to tank farm operations and employees on vapor levels and proposed actions.

The site-wide Tank Vapor Task Team will peer review TRP and WTSS recommendations and issue to the maintenance and operating contractor (i.e., WHC) management recommendations for corrective actions (if required). Possibilities include: no action required; revised administrative controls; remedies for the problem; or installation of a vapor treatment system. This corrective action report will initiate the appropriate documentation, planning, and funding to carry out the recommendations.

Task 1.5.1.1 - Strategy to Relax Supplied Air Requirements

A stated goal of the Vapor Program is to identify a success path that will allow relaxation of supplied air restrictions that currently exist in the tank farms. The requirement that personnel in certain tank farms wear positive pressure breathing apparatus (i.e., use supplied air) was instituted to eliminate the risk of personnel exposures to unknown toxic concentrations released by the waste tanks. This requirement was necessary because a comprehensive industrial hygiene monitoring program had not been completed to evaluate employee exposure. Use of supplied air has been effective in preventing personnel vapor exposures in supplied air zones, but has been both uncomfortable for workers and very costly. The Relaxation of Supplied Air Logic diagram, Figure 4-5, illustrates the process by which IH monitoring data, tank headspace vapor characterization data, and NOAS data will be used.

A detailed description of the strategy to reduce PPE required for tank farm entry has been developed. The revisions will be performed in two steps. The first step involves revision of entry requirements for medium-hazard tank farms. Based on a review of: (1) the area

Figure 4-5. Relaxation of Supplied Air Logic.

monitoring data; (2) a minimum of six source monitoring sweeps; and (3) a minimum of six personal samples that have analyte results less than 10% of the WHC Occupational Exposure Level (based on AIHA [1991] air monitoring strategy), WHC has removed most of the area sampling or supplied air measures for the medium-hazard tank farms involving A, AX, B, S, SX, U, and selected areas in T, TX and TY Farms on a tank farm-by-farm basis.

The second step involves revision of entry requirements for high-hazard tank farms. On June 30, 1993, a strategy similar to the one used in medium-hazard farms was implemented. Using this strategy, recommendations have been made and implemented for reducing the level of monitoring and respiratory protection in BX, BY, and T farms. This effort is ongoing, and recommendations are expected for C, TX and TY farms in third quarter FY 94. However, mandatory requirements for supplied air respiratory protection will remain in effect for all tank farms when entry is made into areas where high levels of vapors are present, or when containment is broken on tanks that are not actively ventilated.

Decisions to revise tank farm entry control measures will be based mainly on information obtained by implementation of an enhanced, routine WHC Tank Farms Industrial Hygiene monitoring program. Key elements of the program have been described in Chapter 6 of WHC-SD-WM-HSP-002, *Tank Farm Health and Safety Plan* (Erickson 1993).

TASK 2.0 - IMPLEMENT ZERO OPTION

This task involves the decision trees that either resolve the safety issue by meeting resolution criteria or derive additional exposure control methods. The first sub-task is to re-evaluate the results from Task 1.0, the collection and analysis of tank headspace samples. Those tanks having headspace constituents below the CES will be considered resolved. Remaining tanks which exceed CES criteria will be evaluated for exposure control methods and revisions will be made as needed to assure worker safety.

If engineered barriers are mandated, then implementation of Task 3.0 mitigation and/or Task 4.0 remediation strategies is warranted. While this strategy addresses tank-by-tank resolution, the goal is ultimate resolution of all tank vapor issues. Upgrades of existing equipment, new treatment systems, continuous monitoring equipment, revised air monitoring programs and revised PPE requirements are the potential products of this task.

TASK 3.0 - IMPLEMENT MITIGATION

If mitigation of tank vapors is required to protect tank farm workers, mitigation approaches will be developed via evaluation of engineering alternatives. These engineering studies for treatment/mitigation options will provide WHC management with solutions and decisionmaking tools. In the event that a vapor treatment system is needed, the design, fabrication, testing and system performance evaluation are logical sub-tasks leading to issue resolution. While mitigation may work in the short term to protect workers, longer-term

remediation may be needed to ultimately solve some vapor issues. The removal of the organic layer from tank 241-C-103 is a good example of a specific type of organic source term mitigation. This does not, however, solve the issue of ammonia generation from the underlying aqueous supernate. Complete remediation, Task 4.0, as removal of all tank contents may be required. After any mitigation effort, the tank headspace must be re-characterized in Task 1.0 to ensure that tank vapors are within established resolution criteria.

TASK 4.0 - IMPLEMENT REMEDIATION

If mitigation, Task 3.0, does not satisfy the goal to resolve tank vapor issues on a tank-by-tank basis, an additional remediation, Task 4.0, may be required to ultimately resolve the generic vapor issues. This may include removal of vapor source layers, removal of all drainable liquid, or complete removal of all tank contents. However, sampling and re-characterization will be required to measure the effectiveness of this solution. Resolution will be affected via Task 2.0, "Zero" Option criteria satisfaction leading to safety issue resolution.

4.2 WORK BREAKDOWN STRUCTURE (WBS)

Specific engineering work plans for each major activity in the Vapor Program list detailed WBSs. The following WBS is a generic approach to the division of labor and responsible organizations.

4.2.1 Site-Wide Tank Vapor Characterization WBS

Site-wide tank vapor characterization will be directed by the Vapor Program.

- Sampling will be performed by WHC/Field Analytical Services (FAS).
- Sample analysis and the initial reports will be performed by OGI, ORNL, PNL, and SNL.

4.2.2 Vapor Release Analysis WBS

- A meteorological station for C tank farm was procured by WHC and will be maintained by PNL.
- The Tank Vapor Database will be developed by PNL and maintained by WHC/TWRS/Characterization.

4.2.3 Industrial Hygiene Work Breakdown Structure (WBS)

Industrial hygiene monitoring will be managed by WHC/ESQ/WTSS and performed by a supporting contractor such as HEHF.

4.2.4 Treatment and Remediation WBS

Treatment and remediation of waste tank vapor problems will be managed by WHC.

4.2.5 Sampling and Analysis WBS

The sampling and analysis of samples for Phases 1 and 2 will be performed by the following groups:

SUMMA® Canisters

- WHC FAS will perform sampling in FY 94.
- OGI, under contract from SNL, will perform the analysis in FY 94.
- PNL will also perform the analysis in FY 94/95 and exclusively in FY 95 with backup by interlaboratory support via Battelle (Columbus) SUMMA® labs.

Multi-sorbent Tubes

- WHC FAS will perform sampling in FY 94/95.
- ORNL will perform analysis in FY 94/95.
- PNL will perform analysis in FY 95 as required.

GC/FID/MS

- WHC/FAC will operate and analyze VSS-generated data in FY-94/95.

Specie-Specific Sorbent Tubes

- WHC FAS to sample.
- PNL to analyze for NPH via OSHA Versatile Sampling method.

4.2.6 Flammability of Tank 241-C-103 Aerosol/Vapors WBS

Resolution of the issue of tank 241-C-103 vapor and aerosol flammability will be performed through a coordinated effort between PNL and WHC.

- WHC/FAS/Waste Tank Safety Programs (WTSP) will document the sampling approach, perform the sampling, and co-author the sampling results report.
- PNL will develop and test the sampling apparatus, analyze the samples obtained, and publish the technical report on the sampling results.

4.2.7 Toxicological Analysis WBS

PNL will select and provide a technical team (TRP) of toxicologists, analytical chemists, and related experts to evaluate the results of vapor data analysis. HEHF will augment the TRP.

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5.0 DESCRIPTION OF OTHER ALLIED ACTIVITIES

5.1 VAPOR RELEASE ANALYSIS

5.1.1 Introduction

One key to preventing further personnel vapor exposures is an understanding of the factors that contribute to vapor releases and place workers at higher-than-normal risk. Past vapor exposure incidents have occurred sporadically, in various locations, during poorly documented weather conditions, and on tanks having unknown vapor leak characteristics. The Vapor Program, through its tank farm-specific analyses of vapor exposure risk factors, will provide an improved understanding of the factors that lead to these incidents. Personnel safety can then be improved through the use of appropriate engineering and procedural controls.

Three related projects have been identified to evaluate the vapor exposure risk factors. First, an individual meteorological station was procured and installed on tank 241-C-103 to gather local meteorological data. Second, a tracer gas study is proposed (in cooperation with SNL/PNL) to evaluate the atmospheric pathways that deliver the tank vapors from the relatively confined tank headspace into the workers' breathing zone. And third, data from the previous two projects, together with headspace characterization data and IH monitoring results, will be compiled and maintained in the VAPORNET database.

5.1.2 Meteorological Stations

Meteorological stations that record the ground-level ambient temperature, barometric pressure, relative humidity, and wind velocity are proposed for installation in each of the Hanford Site waste tank farms. Information obtained from these meteorological stations will be used to monitor the conditions of the individual tank farms. The stations will alarm in the event that conditions favorable to significant vapor releases develop. In the event of a vapor exposure incident, knowledge of the local weather conditions could be invaluable in understanding the incident and preventing future exposures. A single meteorological station has been installed on 241-C-farm as a pilot project.

The use of meteorological stations to gather local, real-time weather data in the tank farms has also been proposed as a part of an overall method to understand vapor behavior in the tank farms. A method for predicting point and path-averaged ambient air volatile organic compound (VOC) concentrations is important to link vapor source emissions and worker vapor exposures. This data will be used by the TRP and WHC/ESQ/WTSS to assess overall risk of vapor exposure in the tank farms. The proposed method is based on establishing the relationship between wind directional frequency and relative vapor concentrations. One - minute averages of wind direction and wind speed will be incorporated into a Gaussian

dispersion model to develop this relationship. Both Fourier transform infrared (FTIR) spectrometry and ambient air sampling are proposed to monitor VOC plumes during field testing of the model.

5.1.3 Atmospheric Pathways Study

Most of the SSTs are currently allowed to breathe passively with the atmosphere and do so with natural barometric fluctuations. Though the bulk of exchanged air probably passes through the HEPA filters on these tanks, some air is exchanged through cracks in the tanks and in piping attached to the tanks. Currently, the release of tank vapors via these cracks is thought to occur, but the extent of vapors released in this manner is speculative. To improve understanding of these releases, a study is proposed in cooperation with PNL using a tracer gas.

The tracer gas study involves the use of an easily detected gas (e.g., helium or sulfur hexafluoride) that is not currently present in the waste tanks. A known quantity of the gas would be released at a specified location in the headspace of a tank, and then a monitoring program would be performed to determine at what locations and times the gas escapes from the tank. Much valuable information will be provided by a tracer gas study, such as the rate at which the gas is mixed in the tank headspace, the transport of gas from a tank to any tanks it is connected with, and the rate at which the gas is lost via the passive ventilation system. A project has been proposed by SNL to perform a controlled release of tank 241-C-102 vapor headspace matrix and analyze it in the area above C-farm by the FTIR method to assess dispersion and dilution patterns.

This task is in abeyance until a need for atmospheric pathways is established.

5.1.4 Vapor Data Base

A vapor database called VAPORNET will be implemented which will serve as the single repository of vapor characterization data. Because a dependence on manual human review of this data has proven inefficient, flagging conditions will be part of the software architecture and execution. Trigger levels of action for toxic vapor levels will be established after quantitative analysis is complete for each class of tank (FeCN, organic, ammonia, etc.). Then a panel of expert toxicologists will identify compounds/constituents of toxicological impact to workers. This target list of chemical vapors will have trip points established based on industrial standards. The software will automatically flag these anomalous conditions and enunciate to the vapor database administrator. These conditions must be recognized and notification actions taken.

After a baseline for tank vapor conditions is established, then actions can be taken to protect workers if anomalous conditions are detected. This detection can come from laboratory analysis of future vapor samples, real time monitoring information from the tank farm

(i.e. continuous air monitors) or feedback from workers while executing work evolutions. A timely review of this data or feedback is an essential element of the goal to adequately protect workers.

Recognition of anomalous conditions, followed by action at the proper level, is the essence of these corrective actions. The VAPORNET database is the primary software engine behind this system and must be updated on a real time basis if the system is to be successful. Any detection of anomalous levels of potentially toxic and/or flammable constituents by laboratory personnel prior to entry into the database will be reported to the Vapor Cognitive Engineer by telephone and notification will be made via urgent cc:Mail to the Manager of Waste Tank Operations. All anomalous vapor conditions detected in tank farms will also be reported as Off Normal conditions in Occurrence Reporting and tracked in that system until resolved. Input of data and management of VAPORNET will be the responsibility of WHC/TWRS Characterization Group in FY 95 and beyond.

5.1.5 Vapor Flow Monitor Design Program

In order to provide early warning of hazardous vapors emanating from passively ventilated underground storage tanks and to minimize potential work expense, an understanding of the behavior of these tanks, which breathe with changes in atmospheric pressure, must be achieved. The principle challenge is to measure and record very small amounts of air flow both in and out of the tank. Unfortunately, the commercially available flow meters require either a large pressure drop or use of a hot wire, and furthermore cannot function at very low flow rates. The potential flammability of Hanford tanks excludes the use of any device that uses a hot wire detector. The flow rates to be measured are motivated by differential pressures of less than .025 cm (0.01 in.) of water and most of the low flow monitors in that range require a minimum differential pressure of 15.2 to 25.4 cm (6 to 10 in.) of water to operate.

To collect the necessary vapor flow data, the Vapor Program has authorized the design of unique flow meters. Two flowmeters are being designed that operate at pressure drops of no more than 2 Pa (0.01 in.) of water and can measure flow rates as low as 1.4 L/min (0.05 ft³/min). One of the flowmeter designs is a very thin impeller rotating on very-low-friction, partial-magnetic bearings. The other design is based on an ultra sensitive differential pressure transducer that is set up to measure the flow induced by pressure differential in a length of pipe. Both of these designs are coupled to a computer that is programmed, after calibration, to display the instantaneous vapor flow. These data then will be recorded. Based on these flow rates, alarms and samplers can be controlled.

5.1.6 Engineering Study For Tank 241-C-103 Vapor Treatment Options

The Engineering Evaluation of Alternatives will be completed in the form of two engineering studies, one non-tank specific and the other specific to tank 241-C-103. The objectives of these studies are described below.

- First, a tank-specific engineering study will be performed, when appropriate data is available, that will select the best alternative for tank 241-C-103. It is intended that this and other follow-on tank specific studies will be performed as required in order to identify a best alternative for a specific tank or vapor event. Tank 241-C-103 will be the first tank to undergo such a tank-specific study after the required characterization of the tank vapor and solid/liquid waste is completed.
- Then, a non-tank-specific engineering study will be performed that will identify and evaluate potential alternatives for mitigating worker exposure to SST vapors. This study is intended to be periodically updated and used as a guide and reference for future tank-specific engineering studies.

This scope of work is an interim step to determine the need for treatment of tank 241-C-103 emissions. This work is a prerequisite to the design, fabrication, and operation of a vapor treatment system as specified in TPA Milestone M-40-07 and Safety Initiative 2N.

5.2 WORKER SAFETY

Worker safety is the first priority for all work performed in the tank farm complex. Many hazards exist in the tank farm environment, including radiological and chemical hazards associated with the operation and maintenance of high-level radioactive chemical waste in underground storage tanks. Other occupational hazards associated with tank farm work are electrical and mechanical in nature. Injuries from heat stress, tripping, falling, cuts, abrasions, sprains, and strains also can occur in the tank farm workplace.

Worker safety is a cultural element of the Hanford Site workplace. The goal of safety and IH professionals is to help workers avoid workplace hazards. The Hanford Site is not a zero-risk environment; however, this does not relieve TWRS line management of the responsibility to provide the safest environment possible. TWRS has taken on this responsibility, in part, with the programs described within this program plan and the tank farm site-specific Health and Safety plan. These programs include waste tank vapor characterization, continued vapor screening, and IH monitoring. These efforts will continue until the waste tank contents are remedied, or until these programs are replaced by more comprehensive ones. Until the tank contents have been fully characterized, an aggressive industrial hygiene program involving source, area, and personal sampling is necessary to assess worker safety.

The key element to relieving worker anxieties due to odors in the tank farms is reliable data and information that restores the workers' confidence in the safety and professional IH community. WHC must demonstrate through good science and proactive programs that safety is a primary management concern.

5.3 INDUSTRIAL HYGIENE

Because employees are currently working in the tank farms, interim protective measures were selected to protect employee health. Since both the chemicals and levels present were not defined, a combination of administrative barricades, respiratory protection and monitoring was selected to provide a high level of employee protection during this interim period. These measures have succeeded in protecting employees from harmful vapor exposures, but have caused other problems. The use of supplied air entails use of full-face masks and air hoses, resulting in decreased visibility as well as tripping hazards. During hot weather, supplied air use presents an additional heat load on employees already exposed to high levels of heat stress. A secondary result is decreased work efficiency. The use of monitors has also resulted in decreased work efficiency due to the additional time and scheduling requirements associated with having monitoring technicians available for each farm entry. In summary, both supplied air use and the use of monitoring technicians have increased costs associated with tank farm work, while decreasing work efficiency.

Although full tank characterization will not be completed for some time, the decision was made to conduct IH monitoring of the employee work area to evaluate employee exposure levels. Using the limited information available from current tank characterization efforts, a list of specific chemicals was developed to initiate monitoring efforts. In addition, thermal desorption units were used to provide estimates of the vapor levels for many organic chemicals that might be present. This effort is being conducted by the WTSS organization in WHC/ESQ, and they have developed a plan to assess employee exposure levels. This plan is separate from the tank headspace characterization efforts, although information will be exchanged between these programs. The objective of this monitoring effort is to match the control measures being used to prevent employee exposure to the actual hazards present in the tank farms from vapor releases. As such, this effort will ensure that employee health is being protected while appropriate control procedures are used.

The monitoring program will initially target all SST farms, as they are considered to present the greatest health hazard to workers. Initially, six tank farms have been classified as high-hazard tank farms for vapor exposures. These are tank farms 241-BX, 241-BY, 241-C, 241-T, 241-TX, and 241-TY. Six other tank farms, namely 241-A, 241-AX, 241-B, 241-S, 241-SX, and 241-U, have been classified as medium-hazard tank farms (Harmon 1993).

5.3.1 Noxious Odor Advisory System (NOAS)

Because of past exposure incidents, a high level of employee concern exists over the possibility of exposure to high levels of vapors during work in the tank farms. By completing both tank vapor headspace characterization and industrial hygiene monitoring, employee exposure levels can be assessed, and proper levels of protection can be implemented. As part of this effort by WTSS, meetings will be held with employees to present sampling results and discuss employee concerns relative to vapor exposure in tank farms. Presentation of the sampling data in a easily understood manner, with opportunities for questions, should go a long way toward addressing employee concerns over vapor exposures. Until this has been completed, however, a system developed to provide rapid response to odor concerns will be used. This system, the Noxious Odor Advisory System (NOAS), provides trained technicians who can respond quickly to vapor exposure incidents. This system uses a group of specialists who will quickly respond to any odor reports. The specialists will have area monitors and continuous instrumentation that can be used to determine both the composition and levels of vapors present in an area. The specialists will also utilize a standard methodology to evaluate contaminant levels in the farm, and will take appropriate actions based on the levels observed. Figure 5-1 illustrates the steps to be taken in the event that an odor incident occurs, as well as a sequence for timely resolution of the issue.

The NOAS will help restore tank farm workers' confidence in WHC safety programs until IH monitoring has been completed in tank farms, because the NOAS demonstrates the WHC commitment to address the quality of tank farm environment air. The benefits of NOAS are numerous. It will enhance hazard communications to workers and the DOE customer, and provide for immediate feedback to workers on the conditions in the tank farms. This information, together with safety briefings on vapor events, will help alleviate the anxiety and fear associated with lack of information. NOAS data that is forwarded to WHC senior management and DOE with appropriate timing will allow decision makers to make informed decisions of appropriate proportion to the actual situation, and will preclude the necessity of taking overly conservative measures for lack of data.

5.4 INTEGRATION WITH OTHER PROGRAMS

The Vapor Program will perform safety and health sampling characterization of Hanford Site waste tank headspace vapors in cooperation with several other program-level initiatives that require vapor data for waste tank operations (e.g., core sampling, recovery, treatment or remediation) at the Hanford Site. However, characterization of waste tank headspace vapors for health and safety issue resolution remains the primary goal of the Vapor Program.

The Rotary-Mode Core Sampling Program requires tank vapor information (constituent list and TOC) in support of the requirements of the Rotary Sampling Core Vapor Data Quality Objectives (WHC-SD-WM-SP-003) (Price 1994).

Figure 5-1. Noxious Odor Response Logic.

A coordinated effort has been undertaken with the Ferrocyanide Safety Program to determine potential concentrations of hydrogen cyanide gas (HCN) in certain tanks. This effort requires the selection of a reliable method to detect and measure (quantify) HCN in Ferrocyanide Watch List tanks. The data is intended to address personnel vapor exposure concerns, and will also provide data for studies on the degradation of ferrocyanide in the waste tanks. The Vapor Program will also be coordinating efforts with PNL and WHC/Emergency, Safety, and Quality (WHC/ESQ) to implement field instrumentation for ground-level HCN monitoring.

The Vapor Program efforts to address industrial hygiene concerns are closely allied with the WHC/ESQ campaign to characterize the tank farm workers' environment. The Vapor Program complements and provides crucial source characterization data to the WHC/ESQ and NOAS programs.

The Vapor program will perform vapor sampling and analysis, as requested by the Flammable Gas Tank Safety Program, to assess levels of methane and organic vapors in the Flammable Gas Watch List tanks. This will be done as opportunities arise to collect samples during other scheduled tank work.

Finally, Vapor Program sampling personnel have worked with the Organic Safety Program to successfully obtain liquid samples from tank 241-C-103. Liquid sampling and analysis were governed by a DQO (Wood et al. 1993). The analysis of these samples included headspace volatile organic compound analyses that supplement the tank vapor analysis. The Organic Safety Program will also evaluate the use of vapor fingerprinting as a means of determining potential risks from organic chemical-containing waste tanks. Support for this effort, if required, will be provided by the Vapor Program.

6.0 PROGRAM SCHEDULE AND MILESTONES

The program schedule and milestones are in the Waste Tank Safety Operations 1993 fiscal year work plan.

WASTE TANK VAPOR RESOLUTION MILESTONE STATUS REPORT																								
MDS #	TPA/SL	FDS #	DATE	FIC	1994												1995							
					Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May
TW2-94-487		1N2H81	12/2/93	NA	▲ Complete field work associated with flammability vapor sampling of C-103																			
TW2-94-471	SI-2i	1N2H81	1/31/94	NA	▼ Resolve flammability issues associated with C-103																			
TW2-94-486		1N2H81	2/18/94	NA	▲ Complete field work associated with Phase 2 vapor sampling of C-103																			
TW2-94-477		1N2H81	2/28/94	NA	▲ Semi-quantitative analysis by PNL of vapor samples from C-103 (Phase 2)																			
TW2-94-478		1N2H81	5/31/94	6/23/94	▲ Quantitative analysis by PNL of vapor samples from C-103 (Phase 2)																			
TW2-94-489		1N2H81	5/31/94	6/23/94	▲ Quantitative analyses by SNL/OQIST of vapor samples from C-103 (Phase 2)																			
TW2-94-494	SI-2m	1N2H81	6/30/94	NA	▼ Complete vapor sampling characterization of C-103 (Phase 2)																			
TW2-94-475	SI-2n	1N2H82	6/30/94	NA	▼ Evaluation of EEA for treatment of C-103 vapor space																			
TW2-93-322	M-40-06	1N2H81	8/31/94	6/30/94	⊙ Complete vapor sampling characterization of C-103 (Phase 2)																			
TW2-94-473		1N2H81	9/30/94	NA	△ Enhance PNL SUMMA lab capability																			
TW2-94-474		1N2H81	9/30/94	NA	△ Enhance multi-carbon tube analysis at ORNL																			
TW2-94-479		1N2H81	9/30/94	NA	△ Complete Phase 3 vapor sampling & char. of suspect tanks																			
TW2-94-480		1N2H81	9/30/94	NA	△ Annual report of vapor sampling																			
TW2-94-488		1N2H81	9/30/94	NA	△ Complete field work of Phase 3 vapor sampling																			
TW2-94-476		1N2H82	9/30/94	NA	△ Operation of a tank vapor flow monitor device for C-103																			

Project: Milestone Status Report Date: 4/27/94	COMPLETE: PLANNED:	TPA ⊕ TPA ⊙	HQ ▼ HQ ▼	RL ⊕ RL ⊕	KEY ▲ KEY ▲
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Figure 6-1. Tank Vapor Milestone Status Report.

Figure 6-2. FY 1994 Waste Tank Vapor Resolution Vapor Sampling Schedule.

	MONTH	DRIVER	TANK	JUSTIFICATION FOR SAMPLING		
				HEALTH & SAFETY	WATCH LIST TANKS	ROTARY CORE
1	COMPLETE		C-103 (SJ#4, 5)	X	ORGANIC	
2	COMPLETE	SI/TPA	C-103 (SJ#6)	X	ORGANIC	
3	COMPLETE	SI/TPA	C-103 (SJ#6B)	X	ORGANIC	
4	CANCELLED Not needed	SI/TPA	C-103 (SJ#6C)	X	ORGANIC	
5	COMPLETE	SI/TPA	C-106	X	HIGH HEAT	X
6	COMPLETE	SI/TPA	C-105	X		CASCADE
7	COMPLETE	SI/TPA	C-104	X		CASCADE
8	COMPLETE	SI/TPA	C-103 (SJ#7A)	X	ORGANIC	
9	5/13-20/94	SI/TPA	C-103 (SJ#7B)	X	ORGANIC	
10	6/20-21/94	SI/TPA	BY-104	X	FeCN	Flam Test 3/28/94
11	6/22-23/94	SI/TPA	BY-105	X	FeCN	4/6/94
12	6/24-27/94	SI/TPA	BY-106	X	FeCN	4/12/94
13	7/11-14/94	SI/TPA	C-108	X	FeCN	Flam Test 7/93
14	7/18-22/94	SI/TPA	C-109	X	FeCN	7/1/94
15	7/26-29/94	SI/TPA	C-111	X	FeCN	8/93
16	8/8-12/94	SI/TPA	C-112	X	FeCN	8/1/94
17	8/15-19/94	SI/TPA	C-101	X		
18	8/22-30/94	SI/TPA	C-102	X		
19	9/5-9/94	SI/TPA	C-107	X		
20	9/12-16/94	SI/TPA	C-110	X		
21	9/26-27/94	SI/TPA	U-111	X	ORGANIC	X
22	9/29-30/94	SI/TPA	U-106	X	ORGANIC	X

Figure 6-3. FY 1995 Waste Tank Vapor Resolution Vapor Sampling Schedule.

	MONTH	DRIVER	TANK	JUSTIFICATION FOR SAMPLING			
				HEALTH & SAFETY	WATCH LIST TANKS	PROBE INSTALLED	ROTARY CORE**
1		SI/TPA	U-107*	X	ORGANIC	X	
2		SI/TPA	TY-101	X	FERROCYANIDE	X	
3		SI/TPA	TY-103	X	FERROCYANIDE	X	
4		SI/TPA	TY-104	X	FERROCYANIDE	X	
5		SI/TPA	T-107	X	FERROCYANIDE	X	
6		SI/TPA	SX-106	X	ORGANIC HYDROGEN	N/A	
7		HISTORY	BX-104	X			
8		SI/TPA	BX-102*	X	FERROCYANIDE	X	
9		SI/TPA	BX-106*	X	FERROCYANIDE		
10		SI/TPA	B-103*	X	ORGANIC	X	
11		SI/TPA	BY-107	X	FERROCYANIDE	X	
12		SI/TPA	BY-108	X	FERROCYANIDE	X	
13		SI/TPA	BY-103	X	FERROCYANIDE	X	
14		SI/TPA	BY-110	X	FERROCYANIDE		
15		SI/TPA	BY-111	X	FERROCYANIDE		
16		SI/TPA	BY-112	X	FERROCYANIDE		
17		SI/TPA	TX-105*	X	ORGANIC		
18		SI/TPA	TX-118	X	FERROCYANIDE ORGANIC		
19		SI/TPA	S-102	X	ORGANIC HYDROGEN		

* Candidates for removal from Watch List in FY 1995

**FY 1995 Rotary Core schedule is unavailable at this time

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