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April 28, 1995

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8. RELEASE STAMP

**DATA QUALITY OBJECTIVES
FOR
GENERIC IN-TANK HEALTH AND SAFETY VAPOR ISSUE RESOLUTION**

April 1995

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LIST OF ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
CES	Consensus Exposure Standard
CGM	Combustible Gas Meter
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy - Richland Operations Office
DQO	Data Quality Objectives
ISS	In Situ Sampling
LFL	Lower Flammability Limit
NIOSH	National Institute of Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
OVS	OSHA Versatile Sampler
PEL	Permissible Exposure Limit
REL	Recommended Exposure Limit
SUMMA®	Registered Trademark for Passivated Stainless Steel Canister
TLV	Threshold Limit Value
TRP	Toxicology Review Panel
USEPA	U. S. Environmental Protection Agency
VSS	Vapor Sampling System
WEEL	Workplace Environmental Exposure Level
WHC	Westinghouse Hanford Company
WDOE	Washington State Department of Ecology

DATA QUALITY OBJECTIVES FOR GENERIC TANK VAPOR ISSUE RESOLUTION

EXECUTIVE SUMMARY

Data Quality Objectives (DQOs) for generic tank vapor and gas sampling were developed in a series of four facilitated meetings and one stakeholder review session, using the most recent U. S. Environmental Protection Agency (USEPA) DQO guidelines. These meetings elicited DQOs for two major vapor problem areas: flammability and toxicity. What follows is a summary of the outputs of the planning team for each of the seven steps of the DQO process. More details regarding the rationale for each of the DQO planning outputs are contained in the DQO document that follows this summary.

Step 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 these tanks. Previous work reports the presence of a fog in some tanks, and the fuel content of the tank gases and vapors may be too high to permit work in these tanks. Numerous reports of adverse health effects associated with vapor exposures in and around tank farms have been made by workers. Confirmed symptoms from these exposure incidents 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 headspace, industrial hygienists can use this information to assess "worst-case" worker exposure levels and focus their industrial hygiene monitoring strategy on these target compounds. Final recommendations on the required level of personal protective equipment 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.

Step 2. Decision Statements

A. Flammability Decision

If the total fuel content of the headspace is $\geq 20\%$ of the lower flammability limit (LFL), then 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. Guideline levels are:

- 10% of the appropriate Consensus Exposure Standard (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.

Step 3. Inputs to the Decision

- 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.

Step 4. 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.

* See 3.2 second paragraph for definition

Step 5. Decision Rules

A. Flammability Decision Rule

If the total fuel content of the headspace equals or exceeds 20% of the LFL for the observed mixture, then stop work and take appropriate actions before resuming sampling or other work on the tank.

B. 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 industrial hygiene 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 industrial hygiene 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 industrial hygiene group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.

Step 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 $LFL_{MIX} < 20\%$.

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.

Step 7. Develop and Optimize the Design for Collecting Data

The Westinghouse Hanford Company (WHC) strategy to resolve the flammability and toxicity issues was approved by the U.S. Department of Energy (DOE) reviewers prior to initiation of this DQO (Gerton, 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.

* * *

In conclusion, the DQO process for generic vapor sampling has been an examination of the strategy used to generate the data needed to adequately characterize the headspace of these tanks. It has proven beneficial because it has offered the stakeholders an opportunity to assess the goals and objectives of the experimental design and comment on the adequacy of the data to support their need. This re-affirmation of the "correctness" of the approach and ultimate data output enhances overall confidence in the data and ultimately in the safety decisions made from these data.

DATA QUALITY OBJECTIVES FOR GENERIC TANK VAPOR ISSUE RESOLUTION

1.0 INTRODUCTION

This document describes the Data Quality Objectives developed for the generic problem of tank vapor characterization. The DQO and sampling and analysis plan previously developed for the pilot tank vapor sampling effort in tank 241-C-103 (known hereafter as C-103) (Osborne 1992) were heavily relied upon for this generic vapor planning effort. The pilot DQOs and vapor sampling and analysis plan were developed prior to these generic vapor DQOs for several reasons. First, tank C-103 represents the worst case for heavy volatile organic vapors and is the greatest challenge for the development of appropriate sampling and analytical methods. Second, it has unique flammable components in its vapor headspace and has been involved in the majority of the vapor exposure incidents at Hanford. Third, a generic DQO was needed to specifically address "lesser" vapor headspace problems in other storage tanks. Fourth, there are 9 other "organic Watch List tanks" which may have similar headspace constituents but in dramatically lesser concentrations. Fifth, there are 20 FeCN class Watch List tanks which may be potential HCN producers. And lastly, 9 other tanks in BX/BY/C farms have a history of vapor incidents associated with them.

These collective 38 tanks comprise the "Suspect Tank List", which is the primary emphasis of the generic DQO. Additionally, the balance of the 177 Hanford tanks need some degree of signature characterization to determine if they meet "suspect tank criteria." The methods determined to be most successful in tank C-103 will be selected for sampling the other Suspect List tanks covered by the generic vapor DQOs contained in this document.

The DQO process starts by describing the problem. In this case, the generic problems associated with vapors in the tank farms were considered. The DQO process was used to lead the planning team through a structured set of steps that help to describe why data are needed, from where and when should data be collected, how data will be summarized and used in support of a decision, and how much uncertainty in that decision can be tolerated. The products of each step of the process are the generic DQOs. These DQOs will be considered on a tank-by-tank basis and used to develop an appropriate sampling and analysis plan designed to generate the right amount and quality of data for decision making. As better estimates of method performance and spatial and temporal variability of vapor constituents become available, the DQOs will facilitate the statistical design and analysis of all vapor data collection efforts that will take place. By specifying DQOs, an important set of criteria are documented that will enable future data users to determine data adequacy and limitations to support decision making.

The primary expectations of the DQO planning team were to build on the previous DQOs and determine the number and types of samples and analyses needed to resolve vapor safety problems for the other Suspect List tanks, and the tank farms in general. It is expected that these generic vapor DQOs will evolve and change with time. As data becomes available from the pilot project vapor sampling system (VSS) sampling event, as subsequent studies address spatial and temporal variability, and as samples are taken from other Suspect List tanks, a better set of historical data will be generated that may affect understanding of the problem and the types and number of samples needed to address the problem. Prior to each new vapor sampling event, these DQOs will be reviewed by the Vapor Program Manager, and any significant changes will be discussed with the appropriate stakeholders to ensure that whenever possible, data adequate for decision making will be generated by the vapor sampling program.

2.0 DQO STEP 1: STATE THE PROBLEM

2.1 BACKGROUND AND SCOPE

The Tank Vapor Issue Resolution Program was established in 1992 to resolve the health and safety issues related to vapors associated with the high-level waste tanks at the Hanford Site. The issues stem from 1) an insufficient understanding of reported exposures of tank farm personnel to unacceptable levels of noxious vapors; and 2) the concern that until the vapors in the waste tanks are well characterized, the risks to worker health and safety cannot be determined.

High-level radioactive waste generated by processes at the Hanford Site has been stored since the mid-1940s in large underground storage tanks which are grouped into tank farms. Due to the variety of 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.

Nineteen vapor exposure events involving 34 workers at the Hanford Site have occurred between July 1987 and May 1993. During these events, workers have reported ill effects including headaches, burning sensation in nose and throat, nausea, and impaired pulmonary function while working around waste tanks on the Hanford project. Musty and foul odors, including the smell of ammonia, have been reported to emanate from several single-shelled tanks (WHC 1994). Ten of these occurrences, involving 18 workers, were linked to C Tank Farm. In particular, tank C-103 was implicated with six of the reported occurrences.

The scope of this generic vapor characterization effort conducted under the Tank Vapor Issue Resolution Program includes two separate characterization and analytical efforts:

- 1) In-tank representative characterization or VSS^(a) and 2) In-tank signature characterization or in situ sampling (ISS).^(a)

In-tank representative characterization involves the headspace vapor sampling process that is evolving at the site, primarily from characterization efforts at tank C-103. This characterization scheme is documented in the Program Plan for the Resolution of Tank Vapor Issues (Osborne 1992). Signature characterization is a characterization program currently under development, and will benefit from the refinement of characterization design based on experience gained through the next few vapor characterization events. As additional information becomes available, the DQO will be updated and revised as needed. As such, this DQO should be viewed as a living document which will evolve with future iterations.

^(a) The vapor sample acquisition methods for these two characterization elements are described in Section 7.6.

2.2 PROBLEM STATEMENTS

2.2.1 Flammability Problem

The presence of flammable constituents in the vapors of Hanford waste tanks is a safety question that must be resolved prior to conducting any type of intrusive sampling, stabilization, or remedial activities in or around the tanks. At issue are the potential effects on the tank and the environment should a fire result from these activities. Standard WHC safety practices dictate that the flammability of the headspace of a tank must be measured and determined to be below 20% of the LFL before intrusive work may be conducted on any Watch List tank. Thirty-three of the 39 "suspect tanks" are on Watch List status.

2.2.2 Toxicity Problem

The major health issue which must be resolved is: Are compounds of toxicological significance present in the tanks at such a level that the industrial hygiene group shall be alerted to their presence so adequate breathing zone monitoring can be accomplished and future activities in and around the tanks can be performed in a safe manner.

2.2.3 Approach to Problem Resolution

The tank-by-tank approach to resolving the vapor headspace issues is to first deal with the potentially catastrophic issue of flammability. Until determinations of headspace LFL are determined, a tank cannot be characterized as having a potential flammable or non-flammable problem which will impact operational and sampling practices. Combustible gas meter readings will be taken to determine the % LFL of the headspace vapor. If these readings indicate any potential problem, samples will be taken to determine the composition and concentrations of flammable constituents in the vapor.

With resolution of the flammability issue, appropriate safe operating procedures will be established and headspace vapors will be sampled to characterize potential human health toxicity of the vapors. Dependent upon the identified vapor constituents and their concentrations, the industrial hygiene group will be advised of the presence of compounds of toxicological significance in a tank headspace. With this information in hand, the industrial hygiene group can devise health and safety procedures that will provide worker protection during subsequent sampling and operational activities. This will include personal monitoring to target compounds detected at levels of concern in the tank and to maximize the effectiveness of monitoring the worker breathing zones around the tanks.

2.3 DQO PLANNING PARTICIPANTS

Implementation of the DQO process for vapor health and safety issues involved management and technical staff spanning a wide range of disciplines, including occupational and environmental safety and health experts, engineers, chemists,

statisticians and DQO facilitators. Table 2-1 presents those personnel who participated in each of the four DQO development meetings. [Washington State Department of Ecology (WDOE) was invited to the planning meetings and received meeting notes, but was not in attendance or available for telephone conferences.] Upon completion of this document, comments will be sought by other stakeholders including DOE, USEPA and the WDOE with the goal of obtaining concurrence from all important data users. The major stakeholders have been kept informed in varying degrees about this program, prior to and during the development of these DQOs.

Table 2-1
Invited Participants in the DQO Development Effort

PARTICIPANT	MEETING DATE				Stakeholder
	12-14-93	01-03-94	01-18-94	02-01-94	Review 02/23/94
<u>WHC:</u>					
J. Osborne, Manager Vapor Program	x	x	x	x	x
J. Huckaby, Engineer		x		x	
T. Rudolph	x				
E. Hewitt	x		x		
P. Morant		x		x	
J. Harbinson		x			
B. Conrad					x
<u>Northwest Instrument Systems:</u>					
M. Story			x	x	x
<u>Hanford Environmental Health Foundation:</u>					
J. Calcagni					x
<u>PNL:</u>					
C. Anderson, Statistician		x	x	x	x
J. Young	x	x	x	x	
D. Mahlum, Toxicologist	x	x	x		
K. Tominey		x	x		
K. Remund, Statistician			x		
B. Pulsipher, Statistician				x	x
P. Turner, DQO Meeting Coordinator	x	x	x		
<u>Neptune and Company:</u>					
D. Michael, DQO Facilitator	x	x	x		x
R. Rytí, DQO Facilitator	x			x	
J. McCann, DQO Facilitator		x	x	x	
<u>DOE-RL:</u>					
S. Branch	x				
P. Hernandez	x				
J. Noble-Dial					x
<u>DOE-GSSC:</u>					
D. Schlick				x	x
<u>WDOE</u>					
M. Lerchen					

3.0 DQO STEPS 2 & 3: IDENTIFY THE DECISIONS TO BE MADE AND INPUTS TO THE DECISION

Two key decisions will be made based on the data collected--a flammability decision and a toxicity decision.

3.1 FLAMMABILITY DECISION

If the flammable gas concentration in the headspace of any tank is greater than 20% of the LFL under steady-state conditions, as measured by the combustible gas meter and/or potential sampling and analysis, then all operational and sampling activity should stop until the problem is investigated and resolved. If the flammable gas concentration in any tank is between 10 and 20% of the LFL in the headspace under steady-state conditions, then work may continue, but a sample will be collected and analyzed to determine the constituents and concentrations of the flammable constituents. If the flammable gas concentration in any tank is less than 10% of the LFL, then operational and sampling work may continue.

3.2 TOXICITY DECISION

If any compounds with toxicological properties exceed their respective trigger points inside the tank, then advise the industrial hygiene group that compounds of toxicological concern are present in the tank headspace. A trigger point is defined as:

- 50% of the appropriate CES concentration for non-carcinogens, and
- 10% of the appropriate CES concentration for carcinogens.

A CES is generally defined as the most stringent of known regulatory or recommended toxicological values for the occupational setting including the threshold limit value (TLV), permissible exposure limit (PEL), recommended exposure limit (REL), and biological exposure limit (BEI). For those constituents with unknown toxicological values, the Toxicology Review Panel (TRP) comprised of toxicologists, industrial hygienists, and occupational medicine physicians will be responsible for development of a CES.

3.3 INPUTS TO THE DECISION

3.3.1 Flammability Decision Inputs

The primary flammability data input will be via combustible gas meter readings, and in some cases, additional determination of the concentration of flammable constituents in the headspace via ISS vapor collection and targeted analysis may be required.

3.3.2 Toxicity Decision Inputs

The following data needs are associated with the toxicity decision:

- Identification of chemical compounds of worker health and safety or toxicological importance in the headspace of the tank.
- Estimates of the concentrations of these toxicologically significant compounds in the headspace.
- Understanding of the toxicological effects of these compounds and the CES for each constituent of concern.

3.3.3 Development of Consensus Exposure Standards

CESs will be generated for each compound of potential toxicological interest detected in the vapor sampling effort. Industrial hygienists have several sources of information for exposure standards against which sampling results may be compared in order to determine whether or not an unacceptable exposure condition exists. A primary source is the American Conference of Governmental Industrial Hygienists (ACGIH) recommended TLVs with some 700 chemicals listed. For compliance purposes, the PELs listed in Subpart Z of the Occupational Safety and Health Administration (OSHA) regulations are used (29 CFR 1910.1000). The National Institute of Occupational Safety and Health (NIOSH) has developed RELs based on recent research and new information about the chemicals, and these RELs are intended for adoption into OSHA regulations. The American Industrial Hygiene Association (AIHA) has also developed Workplace Environmental Exposure Level (WEEL) guides on chemicals for which no current exposure guidelines at the time have been established by other organizations.

In selecting appropriate exposure limits for the chemical constituents in the tank farm headspace vapor, the TRP will first consult the ACGIH TLVs booklet, the OSHA PEL tables, the NIOSH list of RELs, and the AIHA WEELs. The most stringent standard among the above sources will be used.

A chemical may not have published exposure standards. In this case, the TRP can provide a best estimate of the level of acceptable exposure to the chemical. This process for derivation of a consensus exposure limit must rely heavily on professional judgement of the Toxicology Review Panel at Hanford. It may involve an initial literature search in various databases for available information on the chemical. Current data bases may include:

- Registry of Toxic Effects of Chemical Substances (RTECS)
- National Air Toxics Information Clearinghouse (NATICH)
- Integrated Risk Information System (IRIS)
- Gene-Tox Database through the National Library of Medicine
- MEDLINE
- ETIC
- TOXLINE

- CHEMLINE
- Monographs by the International Agency for Research on Cancer (IARC)
- Others as appropriate

Evaluation of health effects may involve a search of information about the chemical or similar analogs on adverse effects, thresholds, possible evidence of carcinogenicity, genotoxicity, developmental toxicity, reproductive toxicity, systemic toxicity, and skin/eye irritation. The no-observable-adverse-effect-level (NOAEL), if available, may be useful for animal-to-human extrapolation. Another numerical value for consideration is the maximum tolerated dose. Generally, factors considered in the toxicity evaluation of a chemical may also include its pharmacokinetic properties, effects on target organs, metabolism (biochemical reaction and transformation), and the rate of absorption and distribution. For example, when considering route-to-route extrapolation, the limitations of extrapolation are clearly apparent and one must account for:

- Difference in absorption efficiency
- Difference in systemic effects
- Occurrence of critical toxic effects at portal of entry
- First-pass effects that may result in either bioactivation or detoxification of a chemical prior to reaching the target organ
- Variations in the time course of target organ concentrations of toxicologically active species

In addition, other factors may include known specific chemical interactions, severity of effects, and other significant effects. The TRP will make various assumptions based on professional judgement to understand toxicological effects for chemicals with little or no known toxicity information. To support the tank farm vapor program, the TRP will apply methods that are scientifically defensible, short of conducting research, to formulate a recommended CES for those chemicals. Insofar as possible, the same approach that AIHA uses in establishing WEELs will be used to evaluate new chemicals.

4.0 DQO STEP 4: DEFINE STUDY BOUNDARIES

Vapor sampling will be eventually conducted on all tanks in the tank farm. This DQO differentiates between 38 of the tanks on the current "Suspect Tank List", tank C-103 (also on the "Suspect Tank List" for which DQOs were developed separately) and all other non-suspect tanks. It further differentiates between those identified as suspect tanks that are actively ventilated, and those that are not.

The spatial boundaries of both the flammability and toxicity decisions for any non-actively ventilated tanks are essentially the internal dimensions of the tank above the level of waste in the tank and not physically inside the dimensions of the riser. This volume is known as the "headspace" of the tank. Due to tank access restrictions that limit access to most of this volume, flammability and toxicity decisions for most tanks will be based on samples taken from a single location at a point approximating the midpoint of the tank volume.

Spatial boundaries for vapor decisions for actively ventilated tanks are the same; however, samples will be collected from the exhaust ventilation headers or stack rather than inside the tanks at some depth below the riser.

Concentrations of constituents in the vapor are not expected to fluctuate greatly over time, and constituents of interest in the vapor are assumed to be homogeneously distributed (well mixed) within the headspace. Accordingly, no effort to consider the time of the year for any tank will be considered. In addition, measurements of vapor constituents from anywhere within the headspace (below the risers) are expected to be representative. If and when results of C-103 samples taken over time and at three depths in the headspace refute these assumptions, the boundaries for the generic vapor DQO will be revisited and the design for sampling will consider these sources of variability.

5.0 DQO STEPS 5: DECISION RULES

The specification of decision rules for each of the identified decisions is a critical step in the DQO process. The decision rule combines the earlier statements into a single statement which specifies how data will be used to make each specified decision. Decision rules for C-103 vapor sampling were adopted for this generic vapor DQO.

5.1 FLAMMABILITY DECISION RULE

The flammability decision rules are stated below. The logic applied to the flammability decision is illustrated in Figure 1.

1. If a single sample of tank vapor fuel content, as measured below the riser with a combustible gas meter (CGM), is greater than 20% of the LFL, then the tank is potentially a flammability hazard and all operational and sampling activity shall cease until the flammability problem is investigated and resolved.
2. If a single sample of tank vapor fuel content, as measured below the riser with a CGM, is 0 to 10% of the LFL, then the tank is not considered a flammability problem and work can proceed.
3. If a single sample of tank vapor fuel content, as measured below the riser with a CGM, is greater than 10% but less than 20% of the LFL, operational and sampling activity may continue under combustible gas monitoring, and sampling will be conducted to determine the vapor constituents and concentrations of the potentially flammable mixture.

Rationale of Decision Rule

The flammability issue for waste storage tanks centers around three potential fuel sources: flammable vapors, flammable floating liquid or interstitial layers and flammable gases (e.g., H_2). This DQO process addresses only the data used to evaluate the flammability of the headspace due to combustible components (i.e., vapors and gases) which may impact the safety of operations. The flammability of a floating liquid or interstitial layer is addressed separately in the Organic USQ DQO document number PNL-8871. Industrial standards for the chemical and gas industries have been adapted for use as guidelines in the Hanford tank farm complex. An additional safety margin has been added to the standard 25% of LFL. The WHC control manual and plant operating procedure level is 20% of LFL. This level is a warning that some condition or process has changed and that some action is needed before operations are continued. The current practice is to measure the LFL and if >20%, then stop work, sample, analyze, and convene the Plant Review Committee (PRC) for review. Their options are to allow continued operation up to some predetermined higher level like 50% LFL or to require dilution or mitigation to reduce the LFL level to below 20% LFL. This logic drives the demand for highly reliable flammability data and a definitive decision rule.

5.2 TOXICITY DECISION RULE

The DQO team established decision rules organizing potentially toxic substances by type to include: the average concentration of any confirmed or suspected human (class A1 or A2) carcinogen, (also teratogens and mutagens), systemic toxins and irritants. The decision rules are specified below. The logic applied to the toxicity decision is illustrated in Figure 2.

1. If the average concentration of any confirmed or suspected human (class A1 or A2) carcinogen, teratogen, or mutagen in a tank headspace is greater than one-tenth of its CES, then advise the industrial hygiene group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.
2. If the average concentration of any systemic toxin in a tank headspace is greater than one-half its CES, then advise the industrial hygiene group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be taken.
3. If the average concentration of any irritants in a tank headspace is greater than one-half of its CES, then advise the industrial hygiene group that compound(s) of toxicological concern are present in the tank headspace so that appropriate worker protection actions can be taken.

Rational for Decision Rule

For the average concentration of any confirmed or suspected human (class A1 or A2) carcinogens, teratogens and mutagens, a 0.1 safety factor is used in lieu of a 0.5 safety factor for irritants and systemic toxicants. These safety factors are based upon current WHC policy(WHC-CM-4-40). It should be noted that complex mixtures of compounds will be evaluated on a case-by-case basis by the Toxicology Review Panel. Grouping of like compounds and the application of mixture rules will be applied the Toxicology Review Panel to generate combined CESs for toxicity assessments.

5.3 DECISION RULE FOR SIGNATURE CHARACTERIZATION OF NON-SUSPECT LIST TANKS

If any compounds of toxicological interest are identified by the Toxicology Review Panel, then classify the problem as either organic or inorganic (e.g., NH_3 , HCN), and collect a more extensive set of samples for representative characterization (see Section 7.6). In general, constituents greater than 10% of their CES will trigger this action. In addition, the Toxicity Review Panel will evaluate the potential adverse effects of complex mixtures as described above, and may request additional samples as appropriate.

FIGURE 1
FLAMMABILITY DECISION LOGIC DIAGRAM

FIGURE 2
TOXICITY DECISION LOGIC DIAGRAM

6.0 DQO STEP 6: LIMITS ON DECISION ERRORS

Limits on decision errors were elicited to provide a criteria against which to measure the expected performance of alternative designs. The DQO planning team decided that the decision errors and corresponding tolerances developed for the tank C-103 DQO effort should apply to the rest of the "Suspect" List tanks. No attempt to specify limits on decision errors for signature characterization events was made by the planning team.

6.1 DEVELOPMENT OF FLAMMABILITY DECISION ERROR LIMITS

The process of specifying limits on decision errors begins by identifying each type of potential decision error and discussing the consequences associated with these error types.

One type of decision error would occur if data indicate that the observed $LFL_{MIX} \geq 20\%$ (flammability is a concern), when the "true" LFL_{MIX} is $< 20\%$ (as determined by additional vapor sampling for any reason). If this occurs, work will be stopped, a safety review will be implemented unnecessarily, and a more complex analysis of LFL will be conducted. These actions would result in the following consequences:

- Increased costs
- Schedule delays
- Possible negative impact on critical path
- Credibility loss.

A second kind of decision error would occur if data indicate that the observed $LFL_{MIX} < 20\%$ (no concern with flammability), when the "true" LFL_{MIX} is $\geq 20\%$. If this occurs, then additional sampling will proceed with sampling methods that could introduce ignition sources to the headspace.

This decision error is of MAJOR CONCERN and has the following consequences:

- Potential negative safety implications
- Increased costs
- Credibility loss (when the correct....)
- Possible continued use of unacceptable operating techniques.

Desired Performance Curve Inputs

After identifying the decision errors and their associated consequences, the planning team considered a series of potential error scenarios (presumed true LFL values) and specified their aversion to these specific potential decision errors in a desired performance (Table 6-1).

Table 6-1
Desired Performance for the Flammability Decision

Presumed true fraction of the LFL	Acceptable probability of deciding to stop work
less than 0.15	$\leq 10\%$
0.15 to 0.20	-
0.20 to 0.50	$\geq 90\%$
more than 0.50	$\geq 99\%$

6.2 DEVELOPMENT OF TOXICITY DECISION ERROR LIMITS

One type of decision error would occur if we observe that the action level (10% of the CES for carcinogens, and 50% of the CES for systemic toxicants and irritants) has been exceeded, when, in fact, the "true action level" has not been exceeded. If this decision error occurs, then worker protection control measures and breathing zone monitoring requirements will be over-prescribed, resulting in the following consequences:

- Increased costs
- Injury or illness to workers resulting from the wearing of personal protection equipment
- Credibility loss
- Scheduled delays.

A second type of decision error would occur if we observe that the action level (10% of the CES for carcinogens, and 50% of the CES for systemic toxicants and irritants) has not been exceeded, when in fact the "true action level" has been exceeded. If this decision error occurs, then workers could potentially be exposed to toxic vapors. This decision error is of major concern and would result in the following consequences:

- Potential worker illness
- Credibility loss
- Increased costs
- Liability to WHC/DOE.

Desired Performance Curve Inputs

Three different sets of constituents were considered independently due to the types of consequences and differences in action levels. Tables 6-2, 6-3, and 6-4 depict the decision error limits established during the DQO development exercise. Since the consequences were most severe for carcinogens, the error tolerances were tightest for these constituents. In all likelihood, these constraints will drive the sampling and analysis design. In fact, the analytical experts predicted that a design adequate to determine if benzene exceeded its CES would be more than adequate to make decisions for all other constituents of concern.

Table 6-2
Desired Performance for the Toxicity Decision:
Average Concentration of Confirmed/Suspected Human (Class A1/A2)
Carcinogenic, Teratogenic or Mutagenic Constituents

Presumed "true" fraction of the CES	Acceptable probability of deciding toxic constituents are present
less than 0.01	≤1%
0.01 to 0.05	≤20%
0.05 to 0.1	-
0.1 to 0.5	≥80%
0.5 to 1	≥95%
1 or more	≥99%

Table 6-3
Desired Performance for the Toxicity Decision:
Systemic Toxicant Constituents

Presumed "true" fraction of the CES	Acceptable probability of deciding toxic constituents are present
less than 0.05	$\leq 1\%$
0.05 to 0.25	$\leq 25\%$
0.25 to 0.5	-
0.5 to 1	$\geq 95\%$
more than 1	$\geq 99\%$

Table 6-4
Desired Performance for the Toxicity Decision: Irritant Constituents

Presumed "true" fraction of the CES	Acceptable probability of deciding toxic constituents are present
less than 0.05	$\leq 1\%$
0.05 to 0.25	$\leq 25\%$
0.25 to 0.5	-
0.5 to 1	$\geq 95\%$
1 or more	$\geq 99\%$

7.0 SAMPLING AND ANALYSIS DESIGNS FOR OBTAINING DATA

7.1 STATISTICAL TERMINOLOGY

The performance tables in Section 6 provide a tool for the decision makers to describe the acceptable probability of making a decision error. The theory behind these tables is based on statistical hypothesis testing, in which the data are used to decide between one condition of the environment (the null hypothesis, H_0) and an alternative condition (the alternative hypothesis, H_A). The null hypothesis is assumed to be true in the absence of strong evidence to the contrary. A decision error occurs when the decision makers are led to believe in one hypothesis when the other is true.

There are two types of decision errors that must be considered. The first type of decision error occurs when the decision makers conclude, based on the data, that H_A is true when, in fact, H_0 is true. This error is sometimes referred to as a false positive, or a Type I, error. When the decision makers specify how often they can tolerate making this type of decision error (e.g. 5 out of 100 times), that is often referred to as the Type I error rate, or α . The second error occurs when the decision makers conclude, based on available data, that H_0 is true when, in fact, H_A is true. This error is sometimes referred to as false negative, or Type II, error. The Type II error rate, or β , is the specification of how often the decision maker can tolerate making this type of decision error.

7.2 DESIGN ASSUMPTIONS

For each vapor sampling event, the flammability and toxicity decision rule will both be addressed. The two assumptions of importance are that the headspace is anticipated to be relatively homogeneous, and that the total study error is approximately equal to measurement error.

7.3 SELECT THE APPROPRIATE STATISTICAL TEST

The hypotheses and statistical tests developed for C-103 heated tube flammability determinations are applicable for generic vapor flammability determinations that are based on the analysis of flammable constituents. For most tanks, the expected value of the CMG is expected to be well below 10% of the LFL. In these cases, a direct comparison of the measured value to 10% of the LFL will be used; hence no statistical test will be conducted.

The hypotheses for the toxicity decision rule for carcinogens are distinguished by a comparison of the average concentrations of confirmed or suspected human (class A1 or A2), carcinogens (this includes teratogens and mutagens) to their corresponding action level (0.1 times the CES for carcinogens). The goal of the testing procedure is to determine if there is sufficient evidence in the collected data to reject the hypothesis that the average concentration of carcinogens is greater than the action level. The

appropriate classical statistical test for resolving this problem is a one sided t-test. The hypotheses can be stated as follows:

H_0 : Mean concentration of each carcinogen ≥ 0.1 times CES

H_A : Mean concentration of each carcinogen < 0.1 times CES.

The desired performance (Table 6-2) indicates that the specified probability of deciding toxic constituents are present at the hypothesis boundary of 0.1 times CES is 0.80. Since this corresponds to making the correct decision when the null hypothesis is true, the probability of making an incorrect decision when the null hypothesis is true (i.e., the probability of deciding H_A when in fact H_0 is true) is one minus 0.80, or 0.20. Thus, the Type I error rate, or α , is 0.20 (i.e., the probability of deciding that toxic constituents are not present when, in fact, they are, is no greater than 0.20). Also indicated is that the probability of deciding to stop work at 0.05 times the CES should be $\leq$ to 0.20. Since this corresponds to making an incorrect decision when the alternative hypothesis is true, the Type II error rate at 0.05 times CES, or β at 0.05 times CES, is 0.20 (i.e., the probability of deciding that the toxic constituents are present when, in fact, they are not, is no greater than 0.20). The region of decision indifference is defined in the desired performance curve at 0.05 to 0.10 times CES.

The hypotheses for the toxicity decision rule for systemic toxins and for irritants are distinguished by a comparison of the average concentrations of systemic toxins or irritants to the action level of 0.5 times its CES. The appropriate classical statistical test for resolving these problems is a one sided t-test. The hypotheses can be stated as follows:

H_0 : Mean concentration of each systemic toxin $\geq 0.50 \times \text{CES}$

H_A : Mean concentration of each systemic toxin $< 0.50 \times \text{CES}$

and

H_0 : Mean concentration of each irritant $\geq 0.50 \times \text{CES}$

H_A : Mean concentration of each irritant $< 0.50 \times \text{CES}$.

The desired performance curves for these decisions are found in Tables 6-3 and 6-4. Using the same discussion as for carcinogens, the Type I error rate, or α , for these constituents is 0.05. The Type II error rate at 0.25 times CES, is 0.25. The region of decision indifference is between 0.25 and 0.5 times CES.

7.4 OBTAIN PERTINENT ESTIMATES OF UNCERTAINTY

No estimates of uncertainty were available for the measurement error for the FC_{Mixture} . As data appropriate for obtaining pertinent estimates of uncertainty become available from C-103, statistical sampling designs will be

considered for other Suspect List tanks. Until that time, professional engineering based designs will be used to obtain samples for decision making.

Estimates of uncertainty for the toxicity decision rule also do not exist at this time. Engineering judgement estimates of the important sources of uncertainty could be obtained, but none of the estimates can be directly tied to observed data.

7.5 POWER ANALYSIS

No power analyses were performed for either the flammability or toxicity decision rules because no prior estimates of uncertainty were available. A retrospective power analysis could provide a useful look at the achievable probabilities of decision error as estimates of uncertainty become available.

7.6 VAPOR SAMPLE ACQUISITION METHODS

Two methods will be used to collect gas and vapor samples for the waste tanks. The primary method employs heated transfer tubing, a heated sampling manifold, relatively sophisticated temperature, flow control, and valving technology, and a vacuum pump to draw air, gases, and vapors out of the waste tanks. Different types of samples can be taken from several stations of the manifold, which is housed with the measurement and control equipment in a climate-controlled mobile laboratory. This method currently requires that a special vapor sampling probe be installed by crane into a riser of the tank. The integrated equipment (e.g., probe, heated transfer tubing, and everything in the mobile laboratory) is referred to as the Vapor Sampling System or VSS.

The VSS was specifically designed to collect representative samples from warm, moist tanks, even if there is a fog in the headspace. Advantages of the VSS include the abilities to perform sampling in adverse weather conditions, to house real-time analytical equipment, and to address high concentrations of organic vapors. Problems yet to be fully addressed include the potential adsorption and loss of certain species on the walls of the transfer lines, and the limitations of a single system to meet the desired sampling schedule.

The second method for collecting gas and vapor samples from the waste tanks is referred to as ISS. Rather than transferring the air, gases, and vapors to be sampled to a remote location, the sampling devices themselves (specifically sorbent traps) are lowered down into the headspace of the tank. This assures representative samples and avoids problems associated with the loss of analytes via wall adsorption.

The ISS method uses simple, inexpensive flow monitoring and control equipment, which currently is mounted on a 2-wheel hand cart. The required equipment is easy to maintain and duplicate. The ISS method provides the ability to collect samples quickly and without the special sampling probe of the VSS. Disadvantages of the ISS method include current limitations on its ability to sample some volatile organic vapors under certain conditions (e.g., acetone in a high-humidity tank) and that each sampling event involves breaking the

containment of the tank. The shipment and analysis of ISS sorbent traps is also currently dependent on proving no radiolytic contamination of the traps has occurred.

A limited ISS event that addresses the most significant noxious gases and vapors, requiring less than 1 hour at an open tank riser, is planned for each single-shell waste tank scheduled for intrusive work, on an opportunistic basis. The opportunistic use of the ISS method is being designed to maximize information obtained while minimizing sampling costs and time. These sampling events are currently designed to collect triplicate sorbent trap samples of ammonia, nitrogen dioxide, nitrogen monoxide, and water vapor. Additionally, triplicate SUMMA canister samples will be collected from the same vicinity as the other samples via an unheated tube, and will be analyzed for volatile organic vapors. Potential radiolytic contamination of the sorbent traps will be addressed by simultaneously collecting a OVS trap for sacrificial radiolytic analysis. The ISS method will also be used to examine several waste tanks for the presence of hydrogen cyanide gas, in support of the Ferrocyanide Tank Safety Program.

7.7 ADAPTIVE ANALYSIS 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 OSHA Versatile Sampling and analysis technology as described in "Aerosol and Vapor Characterization of Tank 241-C-103" (PNL-8875/UC-606) or equivalent will be employed for resolution.

If not, a representative sample of the tank headspace will be taken in a manner that has been shown to be effective to address any documented concerns and the DQOs 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.

This methodology is being employed with respect to tank C-103, and the anticipated dates for accomplishment are:

Representative sampling	January 27, 1994
List of analytes present	February 23, 1994
Identification of analytes of concern	March 1, 1994
Selection of analytical method(s)	March 9, 1994
Modification of methods	June 30, 1994
Quantitative analysis to a known certainty	June 30, 1994

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WHC-SD-WM-DQO-002, Rev. 1

ATTACHMENT A

Data Quality Objectives for Tank Hazardous Vapor Safety Screening

Consisting of 43 Pages Including Introduction

INTRODUCTION:

Any strategy describing the overall approach to safe storage and disposal of waste must identify the problems and decisions requiring characterization data. Requirements for obtaining tank characterization information are developed through the use of the Data Quality Objectives (DQO) process. The DQO process addresses each decision or group of related decisions to specify data needs.

The initial attempt at performing the DQO process to address safety issues revealed points where significant assumptions would be required to proceed. Although the problems and decisions were identified, details of the error tolerances and confidence levels were difficult to develop. Attempts to optimize the data collection for each tank were affected by the limited locations from which samples could be obtained and concerns that samples did not represent overall waste contents. The complexity of sampling made it impossible to design a high confidence data acquisition scheme based solely on multiple samples, and necessitated review of the overall strategy for obtaining data and resolving issues.

A revised safety strategy for the storage of tank waste was developed, focused on ensuring safe operations over a range of waste material rather than on characterizing waste in great detail. The revised safety strategy includes several assumptions about the nature of the waste which require verification through additional sample analysis. Should these assumptions be shown to be well founded, the approach to screening the waste for safety issues and resolving those issues is considerably simplified. The following draft of the data requirements, based on the revised safety strategy, has been prepared.

Clearly any assumptions must be addressed before proceeding with the revised safety strategy. The preceding minor revisions to the baseline DQO document were found to be adequate to perform safety analyses in the near term, while specific additional information needs are pursued to verify the assumptions in the revised safety strategy. In addition to resolving the assumptions, the near term sampling events will obtain information which will support the determination of error tolerances, confidence levels, and optimization schemes in the finalized version of the revised safety strategy DQO. The approach taken in the revised baseline DQO document, simply requesting multiple samples per tank, is the appropriate first step to finalizing the optimization requirements.

The DQO process is iterative in nature. It is anticipated that the data collected in the near term, based on the revised baseline DQO document, will provide the added information needed to provide complete DQO requirements for longer term characterization. As such, the following revised safety strategy DQO may continue to undergo further development and revision as this added information becomes available. At the appropriate time after the revised safety strategy DQO is completed, the necessary reviews and approvals will be conducted and the document will become the new baseline.

WHC-SD-WM-DQO-002, Rev. 1

DATA QUALITY OBJECTIVES FOR TANK HAZARDOUS VAPOR SAFETY SCREENING

J. W. Osborne

April 1995

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DATA QUALITY OBJECTIVES FOR TANK HAZARDOUS VAPOR SAFETY SCREENING

EXECUTIVE SUMMARY

Data Quality Objectives (DQOs) for hazardous vapors were developed using the most recent U.S. Environmental Protection Agency (USEPA) DQO guidelines (EPA QA/G-4, September 1994). Within the general framework of hazardous vapor consideration, two specific vapor problem areas: flammability and toxicity, are addressed. Although these areas are addressed generally in the Safety Screening DQO, more detail is contained in the specific Flammable Gas DQO and contained here in the Tank Hazardous Vapor Safety Screening DQO. What follows is a summary of the outputs of the DQO process for hazardous vapor screening as prescribed by the stakeholders (U.S. Department of Energy [DOE], State of Washington Department of Ecology (Ecology), USEPA, and internal Westinghouse Hanford Company (WHC) customers for vapor data). More details regarding the rationale for each of the DQO planning outputs are contained in the DQO document that follows this executive summary (refer to Figure 1-1 for master DQO logic).

Step 1. Problem Statement

Two potential problems affecting the safe storage of high level radioactive waste at the Hanford Site are: 1) are potential flammable levels of gases and vapors generated or released in waste storage tanks headspace above the 25% LFL level and, 2) is there potential for worker hazards associated with the toxicity of constituents in any fugitive vapor emissions from these tanks? The fuel content of the tank gases and vapors may be too high to permit safe work or continued safe waste storage in or near these tanks. Changes to certain key sentinel gases or vapors in the tank headspace may indicate precursor exothermic reactions. Therefore, it is necessary to baseline the headspace signature before delta changes can be detected. Numerous reports of adverse health effects associated with vapor exposures in and around tank farms have been made by workers. Confirmed symptoms from these exposure incidents 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 as source terms to address potential vapor toxicity and safe storage headspace characterization. If any compounds of toxicological interest are identified in the tank headspace, industrial hygienists can use this information to assess "worst-case" worker exposure levels and focus their industrial hygiene air monitoring strategy on these target compounds. Final recommendations on the required level of personal protective equipment will be based on the worker breathing zone levels of these chemicals. The ultimate goal is to provide safe storage and a healthful workplace in the tank farms complex.

Generation of the required data for 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

Figure 1-1. Logic Diagram for Safety Screening DQO Process.

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acceptable (< 25% LFL) then special in situ sorbent tube bundles can be lowered into the tank. This equipment will be used in subsequent sampling evolutions to: 1) establish concentrations of all flammable headspace constituents; 2) identify compounds of toxicological concern; and 3) quantify compounds of toxicological concern.

Ultimately these data will be used to complete the TPA Milestone M-44 required characterization of the tanks, provide information to guide industrial hygiene air monitoring, provide a design baseline for future or upgraded vapor treatment systems and to provide source term information for estimating fugative air emission inventories.

Step 2. Decision Statements

A. Flammability Decision

If the total fuel content of the headspace is $\geq 25\%$ of the lower flammability limit (LFL), then work must stop until further authorization is given by management. The Plant Review Committee may request additional safety screening to identify the fuel constituents in the tank headspace. This can be accomplished by extended analysis of vapor samples collected and held in reserve from the initial vapor sampling event. This eliminates the need to revisit and resample a tank.

B. Toxicity Decision

If any compounds are detected by the chosen sampling and analytical methods with toxicological properties exceeding their recommended levels inside the tank headspace, then Industrial Health and Safety (IH&S) can make further determinations if additional personal monitoring samples need to be taken to document real exposure situations and assess the adequacy of engineering controls and personal protective equipment. The guideline levels are: at 100% of the appropriate Consensus Exposure Standard (CES)* concentration for all detectable chemicals or .1 ppm which ever is lower.

The principal decision to be made during analysis is the compounds and levels that will be looked for during the analytical procedure. The toxicity decision should be to look for all chemicals detectable by the sampling and analytical methods used that are present above the lower of their CES or 0.1 ppm. Because of the methods used, the data generated for tentatively identified compounds is only semi-quantitative. However, based on the compound specified above, a level of $\pm 50\%$ should be sufficient. Thus, and compound which is estimated to be present at or above 0.1 ppm or the CES for this chemical should be reported to Industrial Health and Safety.

Step 3. Inputs to the Decision

- Initial measurement of tank headspace flammability (CGM based and expressed as % LFL).

*See 3.2 second paragraph for definition

- Identification and quantification of flammable constituents in the headspace (OVM based for TOC concentration and GC/MS based for identification of fuel components).
- Temperature of the headspace and waste.
- Humidity of vapor headspace.
- Identification and quantification of compounds of toxicological importance (GC/MS/IR based data from extended analysis LD > 100 ppb).
- Understanding of the toxicological effects of these compounds and the CES for each constituent of concern (tank vapor database).

Step 4. 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. The tank headspace is assumed to be well mixed based upon convective mixing modeling (Wood and Claybrook) and actual experimental measurement in extended studies of tank 241-C-103. Until further special studies of other single-shell tanks is accomplished, this supposition is considered an assumption based upon modeling and a single tank data set. Vapor sampling from a single point near the centroid of the headspace volume is desirable. Sampling events will be completed in fiscal year 1996 to address diurnal, seasonal, and long-term changes in the vapor and gas concentrations. After the tank's headspace vapor concentration is baselined, periodic monitoring of the tank will be required to identify any delta changes. This information used in conjunction with waste temperature, waste near-surface moisture, and headspace moisture content can provide early warning of changes in tank conditions which might affect continued safe storage.

Step 5. Decision Rules

A. Flammability Decision Rule

If the total fuel content of the headspace equals or exceeds 25% of the LFL for the observed mixture as a instantaneous reading, then stop work and take appropriate actions before resuming sampling or other work on the tank.

B. Toxicity Decision Rule

The toxicity decision rules were specified as follows:

If the average concentration of any detected systemic toxin in a tank headspace is greater than 100% of its CES, or .1 ppm, then advise the industrial hygiene group that a compound(s) of toxicological concern is present in the tank headspace so that appropriate worker protection actions can be assessed.

Step 6. Limits on Decision Errors

A. Flammability Decision Errors

One type of decision error would occur if data incorrectly indicate $LFL^{MIX} < 25\%$

A second kind of decision error would occur if data incorrectly indicate - $LFL^{MIX} < 25\%$

Because the 25% LFL level is an advisory level, it cannot be treated as a absolute action or trigger level.

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.

A third type of error may result if the sampling and analytical methods used do not detect all chemicals present in the headspace.

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.

Step 7. Develop and Optimize the Design for Collecting Data

The Westinghouse Hanford Company (WHC) strategy to resolve the flammability and toxicity issues was approved by the U.S. Department of Energy (DOE) reviewers prior to initiation of this DQO (Gerton, 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.

The specific experimental approach, vapor collection methods, equipment and sampling package configuration, number of samples and type collected and specific analytical procedures are called out in the tank specific Tank Characterization Plan (TCP). The sampling matrix contained in each TCP additionally addresses precision, accuracy, limit of detection and notification limits.

* * *

In conclusion, the DQO process for hazardous vapor sampling has been an examination of the strategy used to generate the data needed to adequately screen and characterize the headspace of these tanks for the purpose of assessing the safe storage conditions of the waste. This process has proven beneficial because it offers the stakeholders an opportunity to assess the goals and objectives of the experimental design and comment on the adequacy of the data to support their need. This re-affirmation of the "correctness" of

the approach and ultimate data output enhances overall confidence in the data and ultimately in the safety decisions made from these data.

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LIST OF ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
CES	Consensus Exposure Standard
CGM	Combustible Gas Meter
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy - Richland Operations Office
DQO	Data Quality Objectives
ISVS	In Situ Vapor System
LFL	Lower Flammability Limit
NIOSH	National Institute of Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
OVM	Organic Vapor Monitor
OVS	OSHA Versatile Sampler
PEL	Permissible Exposure Limit
REL	Recommended Exposure Limit
SUMMA®	Registered Trademark for Passivated Stainless Steel Canister
TLV	Threshold Limit Value
USEPA	U. S. Environmental Protection Agency
VRP	Vapor Review Committee
VSS	Vapor Sampling System
WEEL	Workplace Environmental Exposure Level
WHC	Westinghouse Hanford Company
ECOLOGY	State of Washington Department of Ecology

DATA QUALITY OBJECTIVES FOR TANK HAZARDOUS VAPOR SAFETY SCREENING

1.0 INTRODUCTION

This document describes the Data Quality Objectives developed for the screening of the hazardous tank headspace vapors. Tank 241-C-103 and the other Watch List tanks represent the "worst" challenge for heavy volatile organic and ammonia vapor characterization. There are 18 FeCN class Watch List tanks, 19 organic Watch List tanks, and 14 other tanks in BX/BY/C farms which have a history of vapor incidents associated with them. These collective 43 tanks comprise the Suspect Tank List.

Two classes of chemicals (organics and ammonia) are the principal drivers for the development of appropriate sampling and organic/inorganic analytical methods. A screening DQO was needed to specifically address "lesser" vapor headspace problems in other storage tanks and to focus on non-organic sentinel gases like NH_3 and N_2O , CO_2 , CO and N_2O . For instance, there are now four other "organic tanks" which may have similar headspace constituents to organic Watch List tanks but in dramatically lesser concentrations. These organic signatures and their long-term stability may be important sentinels for tank safety.

The group of tanks covered by this DQO are the remaining unsampled passively ventilated single-shell tanks. Safe storage screening and characterization of these "lesser tanks" to some degree is needed to determine if they meet or exceed safety screening criteria and to properly categorize them for health and safety reasons (i.e., primary NH_3 tank). The methods developed for the characterization of Suspect List tanks will be used to screen (i.e., EPA TO-12) and fully characterize (i.e., EPA TO-14) these tanks as needed.

The DQO process starts by describing the problem. In this case, the two problems associated with vapors in the tank farms were considered. The DQO process was used to lead the DQO team through a structured set of steps that help to justify why data are needed, from where and when should data be collected, how data will be summarized and used in support of a decision, and how much uncertainty in that decision can be tolerated in relation to overall tank safety risk assessment. The products of each step of the process constitute the hazardous safety screening DQO. This DQO will be considered on a generic tank basis and used to develop an appropriate tank specific Tank Sampling Plan designed to generate the right amount and quality of data for decision making on that particular tank (see detailed logic in Figure 1-2 and Figure 1-3). As better estimates of method performance and spatial and temporary variability of vapor constituents become available, the DQO will be the vehicle to revisit the statistical design and modify the analytical approach and sampling methods of all vapor data collection efforts that will take place in the future. By specifying a DQO, an important set of criteria are established that will enable a technical review group to determine data adequacy and limitations to support decision making.

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

Figure 1-3. Overview of Waste Tank Safety Issue Resolution Logic. (2 of 2)

The primary expectations of the DQO planning team were to adapt the approach and methods from previous DQOs and determine the right number and types of samples and analyses needed to screen for vapor safety problems for tank farms in general. It is expected that this vapor safety screening DQO will evolve and change with time. As data becomes available from 1) the characterization of suspect tanks which are governed by the In-Tank Generic Vapor DQO 2) routine use of the in situ vapor system (ISVS), and 3) subsequent studies address spatial and temporal variability, the nature of tank headspaces and their dynamics will come into better focus. This will enhance our understanding of the tank characterization problem and types/number of samples needed to address the problem. Prior to each new vapor sampling event, each sampling and analysis plan will be reviewed by the Vapor Program Manager, and any significant changes will be discussed with the appropriate stakeholders to ensure that whenever possible, data adequate for decision making will be generated by the vapor sampling program.

2.0 DQO STEP 1: STATE THE PROBLEM

2.1 BACKGROUND AND SCOPE

The Tank Vapor Issue Resolution Program was established in 1992 to resolve the health and safety issues related to vapors associated with the high-level waste tanks at the Hanford Site. The issues stem from 1) an insufficient understanding of reported exposures of tank farm personnel to potentially unacceptable levels of noxious vapors; and 2) the concern that until the vapors in the waste tanks are well characterized, the risks to worker safety (flammable conditions) cannot be determined.

The charter of the Vapor Program has been extended to include the overall characterization of the vapor headspace of all passively ventilated single-shell tanks. This data is needed to complete TPA Milestone M-44 tank characterization. For this purpose, Ecology requires reporting of tank headspace source term levels of some 400+ hazardous chemicals listed in the Washington Administration Code. Additionally, information is needed by the Air Emission Inventory DQO to assess potential levels of tank source terms for Clean Air Act air permitting and inventory estimates.

High-level radioactive waste generated by processes at the Hanford Site has been stored since the mid-1940s in large underground storage tanks which are grouped into tank farms. Due to the variety of 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. Likewise, each tank has a unique vapor matrix.

Twenty three vapor exposure events involving 40 workers at the Hanford Site have occurred between July 1987 and February 1995. During these events, workers have reported ill effects including headaches, burning sensation in nose and throat, nausea, and impaired pulmonary function while working around waste tanks at the Hanford project. Musty and foul odors, including the smell of ammonia, have been reported to emanate from several single-shelled tanks (WHC 1994). Ten of these occurrences, involving 18 workers, were linked to C Tank farm. In particular, tank C-103 was implicated with six of the reported occurrences.

The scope of this hazardous vapor screening effort conducted under the Tank Vapor Characterization Program includes two separate characterization sampling strategies: 1) The first involves the physical collection of vapor samples from outside the tank by transporting the vapor via heated sampling lines to the VSS system* and, 2) the second uses an in situ vapor sampling assembly inside the tank headspace using an ISVS* system.

VSS representative characterization involves the headspace vapor sampling process that was pioneered and developed at the site, primarily from characterization efforts at tank C-103. This characterization method (VSS) is documented in the Program Plan for the Resolution of Tank Vapor Issues

*The vapor sample acquisition methods for these two characterization elements are described in Section 7.6.

(Osborne 1994). Vapor signature characterization is a characterization method (ISVS) currently planned for deployment, and is the result of refinement of characterization design based on experience gained through the 57 vapor sampling events. As additional information becomes available, the DQO will be updated and revised as needed. As such, this DQO should be viewed as a living document which will evolve with future iterations.

2.2 PROBLEM STATEMENTS

2.2.1 Flammability Problem

Does the vapor headspace exceed 25% of LFL? If so, what are the principal fuel components?

The presence of flammable constituents in the vapors of Hanford waste tanks is a safety question that must be resolved prior to conducting any type of intrusive sampling, stabilization, or remedial activities in or around the tanks. At issue are the potential effects on the tank and the environment should a fire result from these activities. Standard WHC safety practices* dictate that the flammability of the headspace of a tank must be measured and determined to be below 25% of the LFL before intrusive work may be conducted on any Watch List tank. This DQO addresses the initial safety of conduct of operating flammability measurement. It also addresses the extend fuel component identification and quantification from high flammable conditions (i.e., > 25% LFL).

2.2.2 Toxicity Problem

Are compounds of toxicological significance present in the tanks at such a level that the industrial hygiene group shall be alerted to their presence so adequate breathing zone monitoring can be accomplished and future activities in and around the tanks can be performed in a safe manner?

2.2.3 Approach to Problem Resolution

The tank-by-tank approach to resolving the vapor headspace issues must first address the potentially catastrophic issue of high flammability. Until initial headspace LFL is determined, a tank cannot be fully sampled and characterized. Combustible gas meter readings will be taken to determine the % LFL of the headspace vapor. If these readings indicate any potential problem, vapor headspace samples will be taken to determine the composition and concentrations of flammable constituents in the vapor.

With resolution of the actual flammability condition in a given tank headspace, appropriate safe operating procedures will be established and headspace vapors will be sampled to characterize potential human health toxicity of the vapors and further assess the long-term storage criteria. Dependent upon the identified vapor constituents and their concentrations, the industrial hygiene group will be advised of the presence of compounds of toxicological significance in a tank headspace. With this information in hand, the industrial hygiene group can devise health and safety procedures

*Derived from National Fire Protection Association LFL guidelines.

that will provide worker protection during subsequent sampling and operational activities. This will include personal monitoring to target compounds detected at levels of concern in the tank and to maximize the effectiveness of monitoring the worker breathing zones around the tanks. Additional long-term permanent engineering controls may then be designed based upon the characterization data to provide an ultimate barrier between the source and the worker.

The objective of this screening is not to determine the levels of all vapors present in the tank headspace, or even the levels of all vapor known to have toxic properties. Rather, it is to evaluate the levels of certain toxic vapors that are identified by the sampling and analytical methods chosen. The objective of this DQO is thus to specify which "certain" vapors need to be looked at. These are referred to as "target analytes of toxicological interest" (see Table 2-1).

Table 2-1. Target Analytes of Toxicological Interest

Compound	Sample Type
Acetone	SUMMA TM TST
Acetonitrile	SUMMA TM TST
Ammonia	Sorbent Trap
Benzene	SUMMA TM TST
1,3-Butadiene	SUMMA TM
Butanal	SUMMA TM TST
n-Butanol	SUMMA TM TST
n-Dodecane	OVS CCT
n-Hexane	SUMMA TM TST
2-Hexanone	SUMMA TM TST
Methylene Chloride	SUMMA TM TST
Nitric Oxide	Sorbent Trap
Nitrogen Dioxide	Sorbent Trap
Nitrous Oxide	SUMMA TM
Propanenitrile	SUMMA TM TST
Sulfur Oxides	Sorbent Trap
Tributyl Phosphate	CCT
n-Tridecane	OVS CCT
Vinylidene Chloride	SUMMA TM TST

Because the sampling methods chosen are not guaranteed to collect all vapors, this sampling effort should be considered a screening to determine if chemicals identified by the method are present at sufficient levels to pose a threat to employee health if allowed to escape from the tank. Although the level of vapors present outside of the tank is likely to be much lower than those observed inside the tank, a worst case assumption would be that vapors present outside the tank are at the same level as those inside the tank. Thus, it would appear that it should only be necessary to look for those chemicals identified by the method that are present above their consensus exposure standard (CES) level.

However, since most of the chemicals with identified CES levels have relatively high values (ppm to hundreds of ppm), setting a threshold of the CES would severely limit the amount of data obtained from the sampling and analytical process. On the other hand, lowering the threshold level does not significantly add to the analytical complexity and value until this level drops below about 0.1 ppm. For this reason, all chemicals which are identified by the sampling and analytical methods at either their CES level or 0.1 ppm, whichever is lower, will be evaluated. This should avoid unnecessary analytical costs looking for compounds of low toxicity at ppb levels, while ensuring that compounds with low CES levels are looked for at the CES level.

If chemicals with very low CES (ppb range) are identified by analytical methods and are on the target analyte list, i.e., benzene (CES = .1 ppm) then extended analysis will be conducted in this region of the spectrum down to a 100 ppb limit of detection. This extended analysis will be by exception. The data generated by this effort will be given to Tank Farm IH&S to assist them in their efforts to protect the health of employees working in the tank farms. While the analytical results from this effort will be utilized by IH&S in evaluating the potential for employee exposure to toxic chemicals, they will not be used to set control measures or implement personal protective equipment. This is due to two factors, both of which were noted above. First, the analytical results will not represent all possible toxic substances present in the tanks. Second, the levels measured in the tank headspace are not likely to represent employee exposure levels. The data obtained will thus be a useful tool to assist industrial hygienists in assessing the potential for employee exposures, but will be considered as screening data rather than a complete assessment of all toxic chemicals.

For these reasons, the accuracy of the data is not critical. Even if the results obtained are only within +/- 30%, these data should be sufficient for making industrial hygiene judgments about the need for employee monitoring. The time and money needed to improve sampling and analytical accuracy would not be justified, since no one actually enters the tank headspace, and the vapor levels present outside the tank will have to be reevaluated if the headspace analysis indicates a potential for employee overexposure.

3.0 DQO STEPS 2 & 3: IDENTIFY THE DECISIONS TO BE MADE AND INPUTS TO THE DECISION

Two key decisions will be made based on the data collected--a flammability decision and a toxicity decision.

3.1 FLAMMABILITY DECISION

If the flammable gas concentration in the headspace of any tank is greater than 25% of the LFL under steady-state conditions, as measured by the combustible gas meter and/or potential sampling and analysis, then all operational and sampling activity should stop until the problem is investigated and resolved. If the flammable gas concentration in any tank is between 10 and 25% of the LFL in the headspace under steady-state conditions, then work may continue, but a sample will be collected and analyzed to determine the constituents and concentrations of the flammable constituents. Additional information pertaining to total organic carbon content may be determined in the field (real time) using an organic vapor monitor (OVM). If the flammable gas concentration in any tank is less than 10% of the LFL, then operational and sampling work may continue uninterrupted.

3.2 TOXICITY DECISION

If any compounds with toxicological properties exceed their respective trigger points inside the tank, then advise the industrial hygiene group that compounds of toxicological concern are present in the tank headspace. A trigger point is defined as 100% of the appropriate CES concentration for all chemicals or 0.1 ppm which ever is lower.

A CES is generally defined as the most stringent of known regulatory or recommended toxicological values for the occupational setting including the threshold limit value (TLV), permissible exposure limit (PEL), recommended exposure limit (REL). For those constituents with unknown toxicological values, the WHC Vapor Review Committee (VRC) comprised of toxicologists, industrial hygienists, and occupational medicine physicians will be responsible for development of a CES.

3.3 INPUTS TO THE DECISION

Initial input of historical data on headspace and waste temperature and initial screening data on LFL and headspace humidity will be needed to choose the best sampling method, either VSS or ISVS, for the final characterization. Initial screening will be ISVS based (see Table 3-1 for summary of decision inputs).

Table 3-1. Summary of Decision Inputs.

Decision Input	Decision	Reason for Requesting Decision Input
Vol% hydrogen	1A. Are gases above 25% of the LFL?	Hydrogen is considered to be the major contributor to the flammability of the tank dome space.
Vol% ammonia	1A.	Ammonia is another contributor to the flammability of the dome space.
Vol% methane	1A.	Contributor to flammability.
Vol% CO	1A.	Contributor to flammability.
[Ammonia]	1B. Are gases above noxious vapors limit?	Respiratory and eye irritant.
[CO ₂]	1B.	Simple asphyxiant.
[CO]	1B.	Replaces oxygen in blood.
[NO]	1B.	Respiratory irritant.
[NO ₂]	1B.	Respiratory irritant.
[N ₂ O]	1B.	Respiratory irritant.
Total organic carbon (TOC)	1B.	The presence of TOC in the vapor indicates that other noxious organic vapors could be present.
[Tributyl Phosphate]	1C. Is there an immiscible organic phase?	One of three dominant semivolatile compounds found in past tanks that have been vapor sampled. Indicative of a potential immiscible organic phase in the waste.
[n-dodecane]	1C.	Same as [tributyl phosphate] justification.
[n-tridecane]	1C.	Same as [tributyl phosphate] justification.

[] = Concentrations

The decision inputs summarized in Table 4-1 for decision Steps 1A, 1C, 2, and 3 are referenced in Meacham et al. (1995a). The toxicological compounds from decision Step 1B are referenced in Huckaby and Story (1994).

3.3.1 Flammability Decision Inputs

The primary flammability data input will be via combustible gas meter readings, and in some cases, additional determination of the concentration of flammable constituents in the headspace via an OVM. ISVS vapor collection and targeted fuel component analysis may be required.

3.3.2 Toxicity Decision Inputs

The following data needs are associated with the toxicity decision:

- Identification of chemical compounds of worker health and safety or toxicological importance in the headspace of the tank.
- Estimates of the concentrations of these toxicologically significant compounds in the headspace.
- Understanding of the toxicological effects of these compounds and the CES for each constituent of concern.

3.3.3 Development of Consensus Exposure Standards

CESs will be generated for each compound of potential toxicological interest detected in the vapor sampling effort. Industrial hygienists have several sources of information for exposure standards against which sampling results may be compared in order to determine whether or not an unacceptable exposure condition exists. A primary source is the American Conference of Governmental Industrial Hygienists (ACGIH) recommended TLVs with some 700 chemicals listed. For compliance purposes, the PELs listed in Subpart Z of the Occupational Safety and Health Administration (OSHA) regulations are used (29 CFR 1910.1000). The National Institute of Occupational Safety and Health (NIOSH) has developed RELs based on recent research and new information about the chemicals, and these RELs are intended for adoption into OSHA regulations. The American Industrial Hygiene Association (AIHA) has also developed Workplace Environmental Exposure Level (WEEL) guides on chemicals for which no current exposure guidelines at the time have been established by other organizations.

In selecting appropriate exposure limits for the chemical constituents in the tank farm headspace vapor, the VRC will first consult the ACGIH TLV booklet, the OSHA PEL tables, the NIOSH list of RELs, and the AIHA WEELs. The most stringent standard among the above sources will be used.

A chemical may not have published exposure standards. In this case, the VRC can provide a best estimate of the level of acceptable exposure to the chemical. This process for derivation of a consensus exposure limit must rely heavily on professional judgement of the VRC at Hanford. It may involve an initial literature search in various databases for available information on the chemical. Current data bases may include:

- Registry of Toxic Effects of Chemical Substances
- National Air Toxics Information Clearinghouse
- Integrated Risk Information System
- Gene-Tox Database through the National Library of Medicine
- MEDLINE
- TOXLINE

Evaluation of health effects may involve a search of information about the chemical or similar analogs on adverse effects, thresholds, possible evidence of carcinogenicity, genotoxicity, developmental toxicity, reproductive toxicity, systemic toxicity, and skin/eye irritation. The no-observable--adverse-effect-level (NOAEL), if available, may be useful for animal-to-human extrapolation. Another numerical value for consideration is the maximum tolerated dose. Generally, factors considered in the toxicity evaluation of a chemical may also include its pharmacokinetic properties, effects on target organs metabolism (biochemical reaction and transformation), and the rate of absorption and distribution. For example, when considering route-to-route extrapolation, the limitations of extrapolation are clearly apparent and one must account for:

- Difference in absorption efficiency
- Difference in systemic effects
- Occurrence of critical toxic effects at portal of entry
- First-pass effects that may result in either bioactivation or detoxification of a chemical prior to reaching the target organ
- Variations in the time course of target organ concentrations of toxicologically active species

In addition, other factors may include known specific chemical interactions, severity of effects, and other significant effects. The VRC will make various assumptions based on professional judgement to understand toxicological effects for chemicals with little or no known toxicity information. To support the tank farm vapor program, the VRC will apply methods that are scientifically defensible, short of conducting research, to formulate a recommended CES for those chemicals. Insofar as possible, the same approach that AIHA uses in establishing WEELs will be used to evaluate new chemicals.

4.0 DQO STEP 4: DEFINE STUDY BOUNDARIES

Vapor sampling will be eventually conducted on all passively ventilated tanks in the tank farm complex at Hanford. This DQO differentiates tanks on the current "Suspect Tank List," and all other passively ventilated tanks. It further differentiates between those identified as suspect tanks that are actively ventilated, and those that are not. Because of the active ventilation on all DSTs, their stack sampling and characterization are not included in the scope of the hazardous vapor screening DQO.

The spatial boundaries of both the flammability and toxicity decisions for any non-actively ventilated tanks are essentially the internal dimensions of the tank above the level of waste in the tank and not physically inside the dimensions of the riser. This volume is known as the "headspace" of the tank. Due to tank access restrictions that limit access to most of this volume, flammability and toxicity decisions for most tanks will be based on samples taken from a single location at a point approximating the midpoint of the tank headspace volume. If a case of suspected non-convective mixing arises, the ISVS technology can be adapted to allow vapor samples to be taken at numerous vertical locations through the headspace. This will facilitate a vertical vapor concentration profile to address potential stratification.

Concentrations of constituents in the vapor are not predicted to fluctuate greatly over time (some minor seasonal variation is expected), and constituents of interest in the vapor are assumed to be homogeneously distributed (well mixed) within the headspace. Accordingly, a special study effort to consider the effects of diurnal, seasonal and long-term changes in headspace concentrations will be conducted in FY 1996 to support this supposition. Until these studies are completed on other SSTs, measurements of vapor constituents from anywhere within the headspace (below the risers) are assumed to be representative. If and when results of special studies taken over time and at four depths in the headspace refute these assumptions, the boundaries for this DQO will be revisited and the design for sampling will consider these sources of variability.

5.0 DQO STEPS 5: DECISION RULES

The specification of decision rules for each of the identified decisions is a critical step in the DQO process. The decision rule combines the earlier statements into a single statement which specifies how data will be used to make each specified decision.

5.1 FLAMMABILITY DECISION RULE

The flammability decision rules are stated below. The logic applied to the flammability decision is illustrated in Figure 1-1.

1. If a single sample of tank vapor fuel content, as measured below the riser with a combustible gas meter (CGM), is greater than 25% of the LFL, then the tank is declared a potential flammability hazard and all operational and sampling activity shall cease until the flammability problem is investigated and resolved by the Plant Review Committee.
2. If a single sample of tank vapor fuel content, as measured below the riser with a CGM, is greater than 10% but less than 25% of the LFL, operational and sampling activity may continue under combustible gas monitoring, and samples will be collected from the headspace to determine the vapor constituents and concentrations of the potentially flammable mixture.
3. If a single sample of tank vapor fuel content, as measured below the riser with a CGM, is 0 to 10% of the LFL, then the tank is not considered a flammability risk and work can proceed.

Rationale of Decision Rule

The flammability issue for waste storage tanks centers around three potential fuel sources: flammable vapors, flammable floating liquid or interstitial layers (interim stabilized salt cake tanks which formally held a surface floating organic layer) and flammable gases (e.g., H_2). This DQO process addresses only the data used to evaluate the flammability of the headspace due to combustible components (i.e., vapors and gases) which may impact the safety of operations. The flammability of a floating liquid or interstitial layer is addressed separately in the Organic DQO document number PNL-8871. Industrial standards for the chemical and gas industries have been adapted for use as guidelines in the Hanford tank farm complex. The WHC control manual and plant operating procedure level is the industrially accepted standard of 25% of LFL. This level is a warning that some condition or process has changed and that some action is needed before operations are continued. The current practice is to measure the LFL^(*) and if >25%, then stop work, sample, analyze, and convene the Plant Review Committee (PRC) for review. Their options are to allow continued operation up to some predetermined higher level like 50% LFL or to require dilution or mitigation to reduce the LFL level to below 25% LFL. This logic drives the demand for highly reliable flammability data and a

*National Fire Protection Association recommends that processes be controlled at this LFL %.

definitive decision rule.

5.2 TOXICITY DECISION RULE

The DQO team established decision rules based upon chemical CES and a generic concentration of concern which ever is lower. The decision rule is specified below. The IF/THEN logic applied to the toxicity decision is illustrated in Table 5-1.

If the average concentration of any chemical in a tank headspace is at 100% of its CES or 0.1 ppm, whichever is lower, then the industrial hygiene group will be advised that a compound(s) of toxicological concern is (are) present in the tank headspace. IH&S can then target these analytes for their air monitoring program. Ultimately, data will be generated on the levels of these analytes in the workers' breathing zone. Appropriate worker protection actions can then be taken.

Rational for Decision Rule

For the average concentration of any chemical a 1.0 safety factor is used for irritants, carcinogens and systemic toxicants. It should be noted that complex mixtures of compounds will be evaluated on a case-by-case basis by the VRC. Grouping of like compounds and the application of mixture rules will be applied by the VRC to generate combined CESs for toxicity assessments.

The concentration measurements are for chemicals in the tank headspace not the workers' breathing zone. The industrial hygiene action level concentrations of 50% of CES will be applied to industrial hygiene monitoring data.

If any compounds of toxicological interest are tentatively identified by Phase 1 initial vapor screening, the VRC may classify the problem as either organic or inorganic (e.g., NH_3 , HCN), and require a more extensive extended analyses of the reserved set of samples for representative characterization (see Section 7.6). In general, constituents greater than 50% of their Immediate Dangerous to Life or Health (IDLH) will trigger this action. In addition, the VRC will evaluate the potential adverse effects of complex mixtures as described above, and may request additional samples as appropriate.

Table 5-1. Decision Rule.

Step No.	Decision No.	IF (Decision Threshold)	THEN
1.	1A.	LFLA $\geq$ 25% (LFLA is Lower Flammability Limit Approach - See below for definition)	Implement controls for flammable gas Watch List tank (Schofield 1995). Notify Flammable Gas Safety Program. Continue to next step.
2.	1B.	[Ammonia] $\geq$ 25 ppm AND/OR [CO ₂] $\geq$ 5000 ppm AND/OR [CO] $\geq$ 35 ppm AND/OR [NO] $\geq$ 25 ppm AND/OR [NO ₂] $\geq$ 1.0 ppm AND/OR [N ₂ O] $\geq$ 25 ppm AND/OR [TOC] $\geq$ 1.0 ppm	Restrict workers from area. Go to DQO for Generic In-Tank Health and Safety Vapor Issue Resolution (Osborne 1994a). Notify Noxious Vapor Safety Program. Notify Industrial Hygiene. Continue to next step.
3.	1C.	[Tributyl phosphate] $\geq$ detection limit AND/OR [Dodecane] $\geq$ detection limit AND/OR [Tridecane] $\geq$ detection limit	Implement controls for Organic Watch List tank (Schofield 1995). Go to Organic DQO (Buckley 1995). Notify Organic Safety Program. Continue to next step.
4.	2.	Continuous aqueous layer observed on waste surface.	Tank is under safe storage conditions.* -Monitor waste surface to ensure safe interim storage. -Stop here.

[] = Concentrations

* See (Meacham et al. 1995a).

6.0 DQO STEP 6: LIMITS ON DECISION ERRORS

Limits on decision errors were elicited to provide a criteria against which to measure the expected performance of alternative designs. Decision errors and corresponding tolerances developed for the in-tank generic vapor DQO will apply to the remainder of any new "Suspect" List tanks revealed by safety screening. No attempt to specify limits on decision errors for signature characterization events was made by the planning team.

6.1 DEVELOPMENT OF FLAMMABILITY DECISION ERROR LIMITS

The process of specifying limits on decision errors begins by identifying each type of potential decision error and discussing the consequences associated with these error types.

One type of decision error would occur if data indicate that the observed $LFL_{MIX} > 25\%$ (flammability is a concern), when the "true" LFL_{MIX} is $< 25\%$ (as determined by additional vapor sampling for any reason). If this occurs, work will be stopped, a safety review will be implemented unnecessarily, and a more complex analysis of LFL will be conducted. These actions would result in the following consequences:

- Increased costs
- Schedule delays
- Possible negative impact on critical path
- Credibility loss.

A second kind of decision error would occur if data indicate that the observed $LFL_{MIX} < 25\%$ (no concern with flammability), when the "true" LFL_{MIX} is $> 25\%$. If this occurs, then additional sampling will proceed with sampling methods that could introduce ignition sources to the headspace.

This decision error is of MAJOR CONCERN and has the following consequences:

- Potential negative safety implications
- Increased costs
- Possible continued use of unacceptable operating techniques.
- Credibility loss

Desired Performance Curve Inputs

After identifying the decision errors and their associated consequences, the planning team considered a series of potential error scenarios (presumed true LFL values) and specified their aversion to these specific potential decision errors in a desired performance (Table 6-1).

Table 6-1. Desired Performance for the Flammability Decision

Presumed true fraction of the LFL	Acceptable probability of deciding to stop work
less than 0.15	$\leq 50\%$
0.15 to 0.25	-
0.25 to 0.50	$\geq 90\%$
more than 0.50	$\geq 99\%$

6.2 DEVELOPMENT OF TOXICITY DECISION ERROR LIMITS

One type of decision error—would occur if we observe that the action level (100% of the CES for all chemicals) has been exceeded, when, in fact, the "true action level" has not been exceeded. If this decision error occurs, then worker protection control measures and breathing zone air monitoring requirements may be over-prescribed or misdirected, resulting in the following consequences:

- Increased costs
- Increased risk of injury or illness to workers resulting from the wearing of personal protection equipment in extreme temperature conditions
- Credibility loss
- Scheduled delays.

A second type of decision error would occur if we observe that the action level (10% of the CES for all chemicals) has not been exceeded, when in fact the "true action level" has been exceeded. If this decision error occurs, then workers could potentially be exposed to toxic levels of vapor. This decision error is of major concern and would result in the following consequences:

- Potential worker illness
- Credibility loss
- Increased costs
- Liability to WHC/DOE.

Desired Performance Curve Inputs

Three different sets of constituents were considered independently due to the types of consequences and differences in action levels. Tables 6-2, 6-3, and 6-4 depict the decision error limits established during the DQO development exercise. Since the consequences were most severe for carcinogens, the error tolerances were tightest for these constituents. In all likelihood, these constraints will drive the sampling and analysis design. In fact, the analytical experts predicted that a design adequate to determine if benzene

exceeded its CES would be more than adequate to make decisions for all other constituents of concern.

Table 6-2. Desired Performance for the Toxicity Decision: Average Concentration of Confirmed/Suspected Human (Class A1/A2) Carcinogenic, Teratogenic or Mutagenic Constituents

Presumed "True" Fraction of the CES	Acceptable Probability of Deciding Toxic Constituents Are Present
less than 0.01	$\leq 1\%$
0.01 to 0.05	$\leq 20\%$
0.05 to 0.1	-
0.1 to 0.5	$\geq 80\%$
0.5 to 1	$\geq 95\%$
1 or more	$\geq 99\%$

Table 6-3. Desired Performance for the Toxicity Decision: Systemic Toxicant Constituents

Presumed "True" Fraction of the CES	Acceptable Probability of Deciding Toxic Constituents Are Present
less than 0.05	$\leq 1\%$
0.05 to 0.25	$\leq 25\%$
0.25 to 0.5	-
0.5 to 1	$\geq 50\%$
more than 1	$\geq 90\%$

Table 6-4. Desired Performance for the Toxicity Decision: Irritant Constituents

Presumed "True" Fraction of the CES	Acceptable Probability of Deciding Toxic Constituents are Present
less than 0.05	$\leq 1\%$
0.05 to 0.25	$\leq 25\%$
0.25 to 0.5	-
0.5 to 1	$\geq 35\%$
1 or more	$\geq 50\%$

7.0 SAMPLING AND ANALYSIS DESIGNS FOR OBTAINING DATA

7.1 STATISTICAL TERMINOLOGY

The performance tables in Section 6 provide a tool for the decision makers to describe the acceptable probability of making a decision error. The theory behind these tables is based on statistical hypothesis testing, in which the data are used to decide between one condition of the environment (the null hypothesis, H_0) and an alternative condition (the alternative hypothesis, H_A) the null hypothesis is assumed to be true in the absence of strong evidence to the contrary. A decision error occurs when the decision makers are led to believe in one hypothesis when the other is true.

There are two types of decision errors that must be considered. The first type of decision error occurs when the decision makers conclude, based on the data, that H_0 is true when, in fact, H_A is true. This error is sometimes referred to as a false positive, or a Type I, error. When the decision makers specify how often they can tolerate making this type of decision error (e.g. 5 out of 100 times), that is often referred to as the Type I error rate, or α . The second error occurs when the decision makers conclude, based on available data, that H_0 is true when, in fact, H_A is true. This error is sometimes referred to as false negative, or Type II, error. The Type II error rate, or β , is the specification of how often the decision maker can tolerate making this type of decision error.

7.2 DESIGN ASSUMPTIONS

For each vapor sampling event, the flammability and toxicity decision rule will both be addressed. The two assumptions of importance are that the headspace is anticipated to be relatively homogeneous, and that the total study error is approximately equal to measurement error.

7.3 SELECT THE APPROPRIATE STATISTICAL TEST

The hypotheses and statistical tests developed for C-103 heated tube flammability determinations are applicable for hazardous vapor screening for flammability determinations that are based on the analysis of flammable constituents. For most tanks, the expected value of the CGM is expected to be well below 10% of the LFL. In these cases, a direct comparison of the measured value to 10% of the LFL will be used; hence no statistical test will be conducted.

The hypotheses for the toxicity decision rule for carcinogens are distinguished by a comparison of the average concentrations of confirmed or suspected human (class A1 or A2), carcinogens (this includes teratogens and mutagens) to their corresponding action level (0.5 times the CES for carcinogens). The goal of the testing procedure is to determine if there is sufficient evidence in the collected data to reject the hypothesis that the average concentration of carcinogens is greater than the action level. The appropriate classical statistical test for resolving this problem is a one sided t-test. The hypotheses can be stated as follows:

H_0 : Mean concentration of each carcinogen > 0.5 times CES

H_A : Mean concentration of each carcinogen < 0.5 times CES.

The desired performance (Table 6-2) indicates that the specified probability of deciding toxic constituents are present at the hypothesis boundary of 0.5 times CES is 0.80. Since this corresponds to making the correct decision when the null hypothesis is true, the probability of making an incorrect decision when the null hypothesis is true (i.e., the probability of deciding H_A when in fact H_0 is true) is one minus 0.80, or 0.20. Thus, the Type I error rate, or α , is 0.20 (i.e., the probability of deciding that toxic constituents are not present when, in fact, they are, is no greater than 0.20). Also indicated is that the probability of deciding to stop work at 0.05 times the CES should be < 0.20 . Since this corresponds to making an incorrect decision when the alternative hypothesis is true, the Type II error rate at 0.05 times CES, or β at 0.05 times CES, is 0.20 (i.e., the probability of deciding that the toxic constituents are present when, in fact, they are not, is no greater than 0.20). The region of decision indifference is defined in the desired performance curve at 0.05 to 0.10 times CES.

The hypotheses for the toxicity decision rule for systemic toxins and for irritants are distinguished by a comparison of the average concentrations of systemic toxins or irritants to the action level of 0.5 times its CES. The appropriate classical statistical test for resolving these problems is a one sided t-test. The hypotheses can be stated as follows:

H_0 Mean concentration of each systemic toxin $\geq 0.50 \times \text{CES}$

H_A : Mean concentration of each systemic toxin $< 0.50 \times \text{CES}$

and

H_0 Mean concentration of each irritant $\geq 0.50 \times \text{CES}$

H_A : Mean concentration of each irritant $< 0.50 \times \text{CES}$

The desired performance curves for these decisions are found in Tables 6-3 and 6-4. Using the same discussion as for carcinogens, the Type I error rate, or α , for these constituents is 0.05. The Type II error rate at 0.25 times CES, is 0.25. The region of decision indifference is between 0.25 and 0.5 times CES.

7.4 OBTAIN PERTINENT ESTIMATES OF UNCERTAINTY

No estimates of uncertainty were available for the measurement error for the FC_{mixture} . As data appropriate for obtaining pertinent estimates of uncertainty become available from C-103 and for other Suspect List tanks, revisions to the statistical sampling design will be considered. Until that time, professional engineering based designs will be used to obtain samples for decision making.

Estimates of uncertainty for the toxicity decision rule also do not exist at this time. Engineering judgement estimates of the important sources of uncertainty could be obtained, but none of the estimates can be directly tied

to observed data.

7.5 POWER ANALYSIS

No power analyses were performed for either the flammability or toxicity decision rules because no prior estimates of uncertainty were available. A retrospective power analysis could provide a useful look at the achievable probabilities of decision error as estimates of uncertainty become available.

7.6 VAPOR SAMPLE ACQUISITION METHODS

Two methods will be used to collect gas and vapor samples for the waste tanks. The first method, Type 3 or VSS (see Figure 7-1), employs heated transfer tubing, a heated sampling manifold, relatively sophisticated temperature, flow control, and valving technology, and a vacuum pump to draw air, gases, and vapors out of the waste tanks. Different types of samples can be taken from several stations of the manifold, which is housed with the measurement and control equipment in a climate controlled mobile laboratory. This method currently requires that a special vapor sampling probe be installed by crane into a riser of the tank. The integrated equipment (e.g., probe, heated transfer tubing, and everything in the mobile laboratory) is referred to as the Vapor Sampling System or VSS. Vapor samples are collected either by SUMMA™ canisters or sorbent traps.

The VSS was specifically designed to collect representative samples from warm, moist tanks, even if there is a fog in the headspace. Advantages of the VSS include the abilities to perform sampling in adverse weather conditions, to house real-time analytical equipment, and to address high concentrations of organic vapors. Problems yet to be fully addressed include the potential adsorption and loss of certain species on the walls of the transfer lines. This system is currently used for the collection of vapor samples from all suspect Watch List tanks in fiscal year 1995 and will be held in reserve for special studies of tanks identified by ISVS hazardous vapor screening in fiscal year 1996.

The second and primary vapor screening method, Type 4, for collecting gas and vapor samples from the waste tanks is referred to as In Situ Vapor System (ISVS) (see Figure 7-2). Rather than transferring the air, gases and vapors to be sampled to a remote location, the sampling devices themselves (specifically sorbent trap bundles) are lowered down into the headspace of the tank. This assures more representative sample collection and avoids transport efficiency problems associated with the loss of analytes via wall adsorption. Whole air SUMMA™ canister samples for permanent gas analysis are also collected via this system, but are external to the tank.

The ISVS method uses simple, inexpensive digital mass flow measurement and control equipment, which currently is mounted on a 2-wheel hand cart. The required equipment is easy to maintain and duplicate. The ISVS method

Figure 7-1. Vapor Sampling System

Figure 7-2. In Situ Vapor System

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provides the ability to collect samples quickly and without the special sampling probe of the VSS. Disadvantages of the ISVS method include current limitations on its ability to sample some volatile organic vapors under certain conditions (e.g., acetone in a high-humidity tank) and that each sampling event involves breaking the containment of the tank. The shipment and analysis of ISVS sorbent traps is also currently dependent on proving no radiolytic contamination of the traps has occurred.

A limited ISVS event that addresses the most significant noxious gases and vapors, requiring less than three hours at an open tank riser, is planned for each remaining uncharacterized passively ventilated single-shell waste tank. These sampling events are currently designed to collect triplicate sorbent trap samples of ammonia, nitrogen dioxide, nitrogen monoxide, and water vapor. Additionally, triplicate SUMMA™ canister samples will be collected from the same vicinity as the other samples via an unheated tube, and will be analyzed for volatile organic vapors. Potential radiolytic contamination of the sorbent traps will be addressed by simultaneously collecting a OVS trap for sacrificial radiolytic analysis. If a tank is identified as warm and humid, based upon screening, the VSS may be reactivated to sample and characterize the tank.

7.7 ADAPTIVE ANALYSIS STRATEGY

For the hazardous tank vapor screening analysis, the following adaptive analytical strategy will be employed.

If a flammable safety concern tank is identified by vapor screening, special study in situ sorbent sampling using OSHA Versatile Sampling and analysis technology as described in "Aerosol and Vapor Characterization of Tank 241-C-103" (PNL-8875/UC-606) or equivalent will be employed for resolution.

If the tank is safe to sample, a representative sample of the tank headspaces will be taken in a manner that has been shown to be effective to address any documented concerns and the DQOs for that tank, (SUMMA™ canisters and sorbent tubes). 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 100 parts 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 tentatively identified compounds (TICs) contains any analytes that are of concern to the program; e.g., toxicity, those concerns will be addressed and judged by the VRC 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.

The analytical strategy for hazardous vapor screening is a iterative phased approach. The preferred sample collection method is the Type 4 ISVS cart utilizing a down hole vapor sampling bundle which can collect vapor from any

Comprehensive Hazardous Vapor Safety Screening Program

Sampling Method

- ❖ IVS (Type 4) for 104 passively ventilated single-shell tanks

Sample Distribution

Performing Lab

Analysis

- ❖ Phase 1 screening

Decision Rule

- ❖ Via safety screening, DQO decision gate

Extended Analysis

- ❖ Phase 2 Characterization

Action

Vapor Review Committee (Industrial Hygiene, Toxicology, Industrial Safety, HEHF Occupational Medicine)

Figure 7-3. Comprehensive Hazardous Vapor Safety Screening Program

vertical height between the bottom opening of the riser in the headspace to within millimeters of the waste surface.

The sampling strategy is to collect a complete vapor sample set which can be used to complete the initial hazardous vapor screening and ultimately to complete full definitive characterization of the tank's headspace if warranted. This "standard" sample set is described in Table 7-1.

The concept is to sample a tank once and iteratively analyze the samples to the degree necessitated by the findings. An example is to collect a "standard set" of five NH_3 sorbent traps from each tank. Phase 1 initial screening will analyze two traps as a screening set. If the level of NH_3 is well below the CES (TLV = 25 ppm), then stop analysis and discard the remaining traps. However, if the level is at 50% of IDLH (IDLH = 300 ppm) then additional confirmation analysis of all NH_3 traps is warranted. The strategy allows for additional sample analysis as directed by confidence levels as the action level is approached. Because the maximum number of samples needed were collected during the sampling event, resampling is not needed. Because of the high cost and time penalty for lab analysis, this strategy offers the greatest economy while generating the right amount of data which is defensible to TCP accuracy and precision requirements. This concept is collectively described as "right data at right confidence at minimum time and cost." This logic is depicted in Figure 7-3.

In the case of SUMMA™ canister samples for organics, Phase 1 initial screening will use EPA TO-12 (GC/FID) analysis to assign a TOC level to the tank. If the action level criteria presented in the TCP is exceeded, the VRC/TRC may request additional extended analysis of the sorbent traps for identification of the chemicals which comprise the TOC level. Based upon this information, these groups may again request extension of analysis to use EPA TO-14 (GC/MS/IR) methods to lower the limit of detection to 10 ppb. If the chemical is an analyte of toxicological interest (see Table 2-1), confidence in the data may be achieved by triplicate analysis of the reserved whole air SUMMA™ canister samples.

Table 7-1. Sample Chemical, Physical, And Radiological Analytical Requirements

VAPOR		COMMENTS		SEE TABLE 2 FOR NO. OF SAMPLE/BLANK CONTAINERS							
Plan Number	WHC-SD-WM-TP-335	Type 3 vapor sampling system (VSS) using heated vapor probes.	Early Notify	Organization	WHC	PNL	ORNL				
Generic:	Type 3 Vapor SAP for each tanks listed in section 2.0		Process Control	SUMMA® Canister ^a		X					
Program Contact	J. W. Osborne		Safety Screen	Sorbent Trap System ^b		X					
TWRS Contact	R.D. Schreiber		Waste Management	Triple Sorbent Trap			X				
Lab Project Coordinator	S. C. Goheen (PNL) R. A. Jenkins (ORNL)		RCRA Compliance	HEPA Filter	X						
			Special	Tritium Trap	X						
PRIMARY ANALYSES			CRITERIA							REPORT FORMAT	
ANALYSIS METHOD	PRIMARY ANALYTE	PROCEDURE	LAB	SAMPLE PREP	SAMPLE CONTAINER	SURR SPIKE ^c	NOTIFICATION LIMIT (NL) ^d	EXPECTED RANGE	PRECN at NL	ACCURACY at NL	
EPA TO-14 GC/MS	Organic* Speciation	PNL-TVP-01 PNL-TVP-02 PNL-TVP-03	PNL	Direct	SUMMA®	none	≥ 700 ppmv n-Butanol 50% IDLH for all others*	not available	±25%	70-130%	I, VI
GC/TCD	CO ₂ CO CH ₄ H ₂ N ₂ O	PNL-TVP-05 PNL-TVP-02	PNL	Direct	SUMMA®	none	N/A ≥ 20% LFL ≥ 20% LFL ≥ 20% LFL not available	not available	±25% ±25% ±25% ±25%	70-130%	VI I, VI I, VI I, VI I, VI
IC	NO NO ₂	PNL-TVP-09 PNL-ALO-212	PNL	H ₂ O Extraction	Sorbent Trap	none	≥ 50 ppmv ≥ 10 ppmv	≥ 2 ppmv ≥ 0.1 ppmv	±25% ±25%	70-130%	I, VI I, VI
Gravimetric	H ₂ O	PNL-TVP-09	PNL	Direct	Sorbent Trap	none	N/A	≥ 3 mg/L	±25%	70-130%	VI
Selective Electrode	NH ₃	PNL-TVP-09 PNL-ALO-226	PNL	H ₂ O Extraction	Sorbent Trap	none	≥ 150 ppmv	≥ 2 ppmv	±25%	70-130%	I, VI
GC/MS	Organics**	AC-MM-1-033153 CASD-OP-300-WP03 CASD-OP-300-WP04 CASD-OP-300-WP05 CASD-OP-300-WP06	ORNL	Thermal Desorption	Triple Sorbent Trap	all	≥ 700 ppmv n-Butanol, 50% IDLH for all others**	not available	±25%	70-130%	I, VI
Total α Total β Total γ	Radon Daughters	LA-508-110 LA-508-111 LA-508-162	WHC	Direct	HEPA Filter	N/A	≥60 pCi/g α ≥200pCi/g β ≥200 pCi/g γ	<60 pCi/g α <200 pCi/g β <200 pCi/g γ	±25% ±25% ±25%	70-130%	I, II
Liq. Scin.	Tritium ^e	LA-548-111	WHC	Direct	Tritium Trap	N/A	N/A	not available	N/A	N/A	II
GC/FID	Organics	WHC-IP-1127(4.5)	SML	Direct	On-line	N/A	N/A	N/A	N/A	N/A	II, VI

N/A: Not Applicable

a No extra canisters, except archive, will be stored by PNL.

b System contains individual sorbent media sections for NO_x, NH₃, & H₂O.

c Samples spiked with surrogates.

d Action required if any compound exceed 50% IDLH.

e Survey purpose only.

*Acetone, acetonitrile, benzene, 1,3-butadiene, butanal, n-butanol, n-hexane, methane, propane nitrile. Other organic species detected at levels deemed sufficient by the Toxicology review Panel to be of potential toxicological concern shall be reported following Format I.

**Acetone, acetonitrile, benzene, butanol, n-dodecane, n-hexane, propane nitrile, tributyl phosphate, n-tridecane. Other organic species detected at level deemed sufficient by the Toxicology Review Panel to be of potential toxicological concern shall be reported following Format I.

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