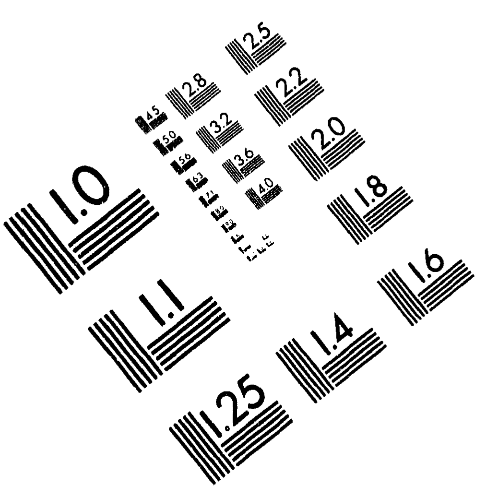

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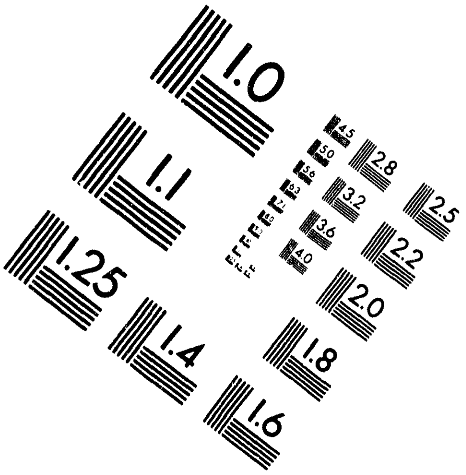

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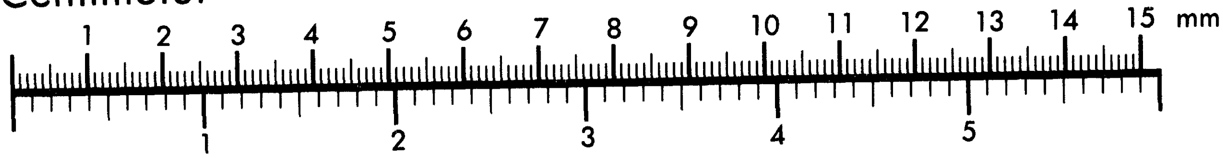

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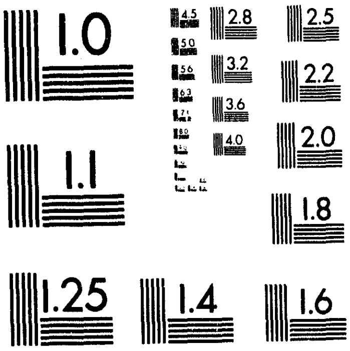

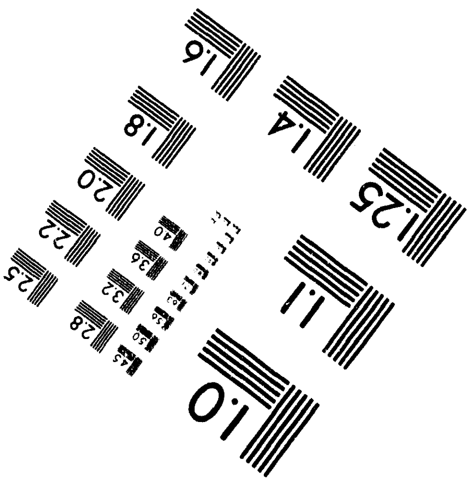

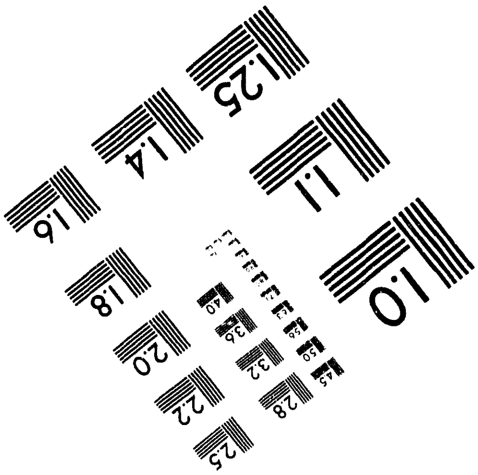

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WHC-EP-0734 Rev. 1
UC-600

Tank 241-C-103 Headspace Flammability

J. L. Huckaby

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LIST OF ACRONYMS

CGM	Combustible Gas Meters
FIC	Food Industries Company
HEPA	High-Efficiency Particulate Air [filter]
LFL	Lower Flammability Limit
NPH	Normal Paraffinic Hydrocarbons
OSHA	Occupational Safety and Health Administration
OVS	OSHA Versatile Sampler
PUREX	Plutonium-Uranium Extraction
RTDs	Resistance Temperature Devices
TBP	Tributyl Phosphate
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

1.1 PURPOSE

Information regarding flammable vapors, gases, and aerosols is presented and interpreted to help resolve the tank 241-C-103 headspace flammability issue. Analyses of recent vapor and liquid samples, as well as visual inspections of the tank headspace, are discussed in the context of tank dynamics.

1.2 SCOPE

This document is restricted to issues regarding the flammability of gases, vapors, and an aerosol that may exist in the headspace of tank 241-C-103. While discussing certain information about the organic liquid present in tank 241-C-103, this document addresses neither the potential for, nor consequences of, a pool fire involving this organic liquid; they have been discussed by Postma et al. 1994.

1.3 BACKGROUND

Concern that the headspace of tank 241-C-103 may contain a flammable mixture of organic vapors and an aerosol of combustible organic liquid droplets arises from the presence of a layer of organic liquid in the tank. This organic liquid is believed to have originated in the plutonium-uranium extraction (PUREX) process, having been stored initially in tank 241-C-102 and apparently transferred to tank 241-C-103 in 1975 (Carothers 1988). Analyses of samples of the organic liquid collected in 1991 and 1993 indicate that the primary constituents are tributyl phosphate (TBP) and several semivolatile hydrocarbons (Prentice 1991, Pool and Bean 1994). This is consistent with the premise that the organic waste came from the PUREX process, because the PUREX process used a solution of TBP in a diluent composed of the n-$C_{11}H_{24}$ to n-$C_{15}H_{32}$ normal paraffinic hydrocarbons (NPH).

At the temperature of the waste surface, the vapor pressure of the PUREX process TBP-NPH solution is known to be far too low to support flame propagation (van Tuyl 1983, Huckaby and Estey 1992). However, if a very dense aerosol of organic liquid droplets were present in the headspace, a flammable condition could exist. The possibility of such an aerosol was supported by reports that the headspace was foggy, and by data from a developmental vapor sampling event in 1989 (Ulbricht 1991, Trent 1990) that was shown to have been experimentally flawed (Story 1992).

A methodology for determining the flammability of the tank 241-C-103 headspace was developed between September and December 1992 by a team of scientists and engineers working for the Tank Vapor Issue Resolution Program. This methodology involved three steps. The first step, performed in November 1993, was an initial evaluation of the concentrations of flammable permanent gases present. The second step, performed in December 1993, was to determine the total concentration of NPH, both in the aerosol and vapor phases, in the tank 241-C-103 headspace. For this, filtered sorbent traps were inserted directly into the headspace to trap the NPH *in situ* (Huckaby 1993).

The November and December sampling events provided direct evidence that the fuel content of the headspace is well below levels of concern. Section 3.0 describes and discusses the sampling results. The November sampling was accomplished by non-intrusive means, drawing tank gases and vapors directly from access ports on two of the tank risers. This sampling method limits the validity of the sampling with respect to condensible and condensate-soluble vapors, but affords a reasonably good analysis of permanent gases such as hydrogen and methane. Results, discussed in Section 3.2, indicate that these gases are at acceptable levels. The initial sampling for NPH, performed in December, revealed that the current NPH concentration in the headspace is far below levels of concern for flammability. The December sampling event also established that no aerosol was visibly present in the headspace.

The third step to resolve the tank 241-C-103 headspace flammability issue, begun in January 1994 but planned to continue throughout the year, requires that representative samples be collected from the headspace for determining the concentrations of flammable gases and volatile organic species, as well as further analyses of semivolatiles such as NPH. The sampling events are planned to characterize the toxicologically significant species in tank 241-C-103, but will also serve to ensure seasonal variations do not significantly affect the conclusions of this report.

1.4 DATA QUALITY

This report discusses both historical and recent vapor and aerosol data. Historical data is deemphasized in this report, since the quality of the data has been an issue (e.g., Ulbricht 1991 and Story 1992). Recent data, obtained in 1993 and 1994, has been collected by the Tank Vapor Issue Resolution Program in accordance with *Tank 241-C-103 Vapor and Gas Sampling Data Quality Objectives* (Osborne et al. 1994), at the Westinghouse Hanford Company (WHC) Safety and Quality impact level 3 (Huckaby 1993, Conrad 1993).

2.0 HEADSPACE CONDITIONS

2.1 TANK DESCRIPTION

Tank 241-C-103 is a 1.9-ML (530-kgal), high-level nuclear waste storage tank. Constructed in 1943-1944, it has a single, 22.9-m (75-ft)-diameter mild steel liner supported by reinforced concrete and a reinforced concrete dome. The dome supports 11 steel pipe risers through which the tank contents may be accessed. Figure 2-1 depicts the arrangement and schedule of tank 241-C-103 risers, and the locations of the 3 concrete access pits. As shown in Figure 2-2, tank 241-C-103 is also directly connected to tank 241-C-102 by a buried, 7.6-m (25-ft)-long, 7.6-cm (3-in.)-diameter cascade line. When tank 241-C-102 was full, the cascade line allowed the overflow of liquid to tank 241-C-103. A similar cascade line connects tanks 241-C-101 and 241-C-102.

Currently, tank 241-C-103 contains approximately .738 ML (195 kgal) of sludge and aqueous liquid waste (Hanlon 1994), as calculated from a measured waste depth of 168 cm (66 in.) In addition, tank 241-C-103 has a floating layer of organic liquid waste (immiscible in the aqueous waste) determined to be between 3.8 and 5 cm (1.5 and 2.0 in.) thick in December 1993. A Food Industries Company (FIC) automatic level gauge, mounted on riser #8, is used to determine the aqueous waste surface, by conductivity, on a weekly basis.

The relative stability of the waste surface level in tank 241-C-103 is an indication that the tank does not undergo periodic venting of gases from the stored waste. Burke (1991) has charted the surface level data from tank 241-C-103 between 1980 and 1991. The data indicate a decrease in the surface level of the tank of about 4 cm (1.6 in.) over the 11-year period, which Burke attributes to the evaporation of water. Deviations from the running baseline level are indicated to be on the order of tenths of an inch, or at about the resolution of the level gauge itself. Though the level gauge data is not recorded continuously, there is no evidence tank 241-C-103 is undergoing episodic gas release events. This issue has been addressed in a safety assessment by Postma et al. (1994).

2.2 HEADSPACE CONVECTION

The headspace of tank 241-C-103 is expected to be mixed by convective air currents. Radioactive decay occurring within the waste generates heat that is transferred in all directions from the tank. The waste surface is thus warmer than the concrete dome, resulting in the upward convection of air warmed by the waste surface and downward convection of air cooled by the concrete dome. According to a model developed by S. A. Wood (1992) to describe the headspace of a similar situation in tank 241-C-109, warm air rises in the central region of the tank, flows outward along the dome, and falls at the tank wall.

Figure 2-1. Tank 241-C-103 Riser Locations.

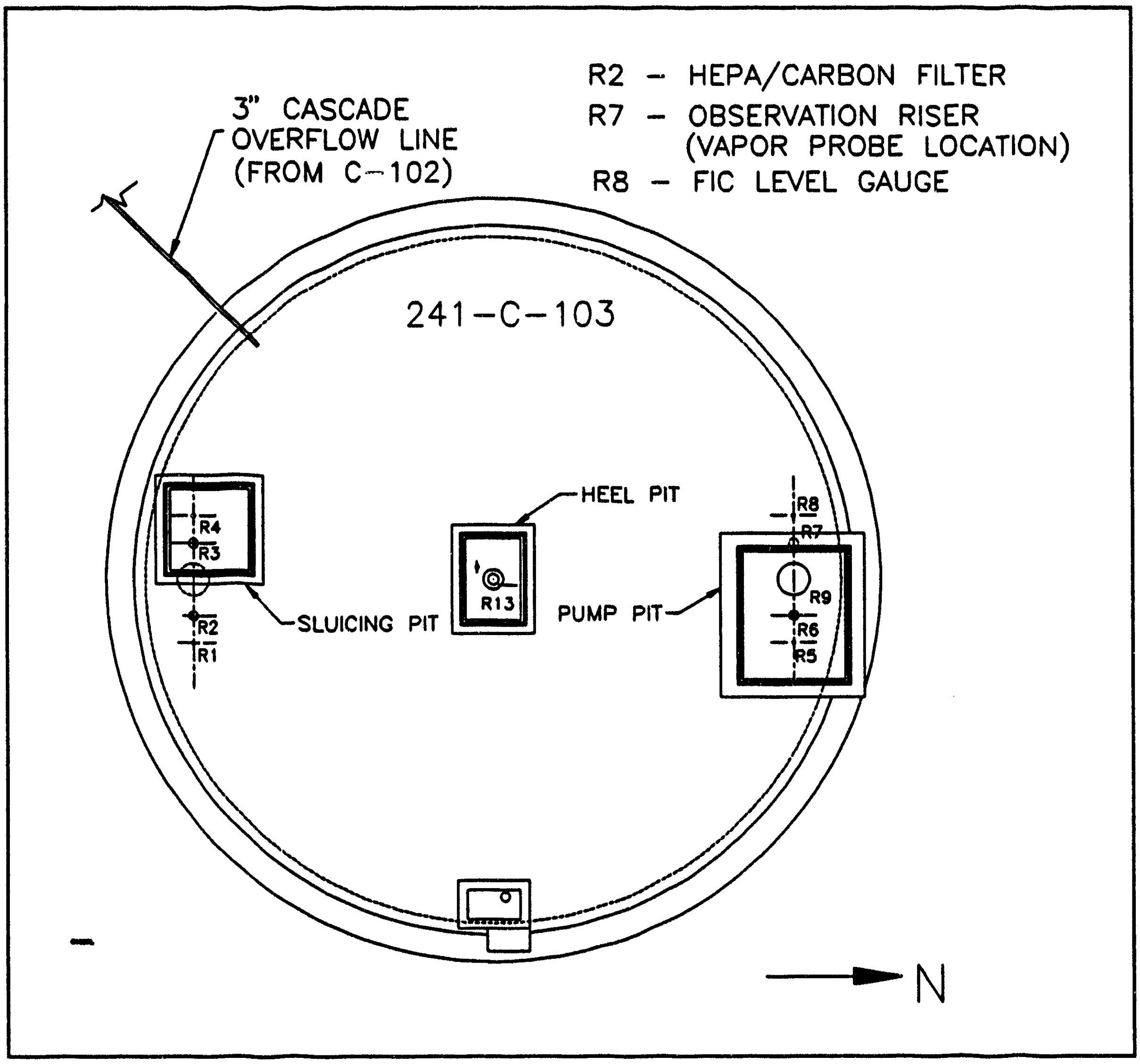
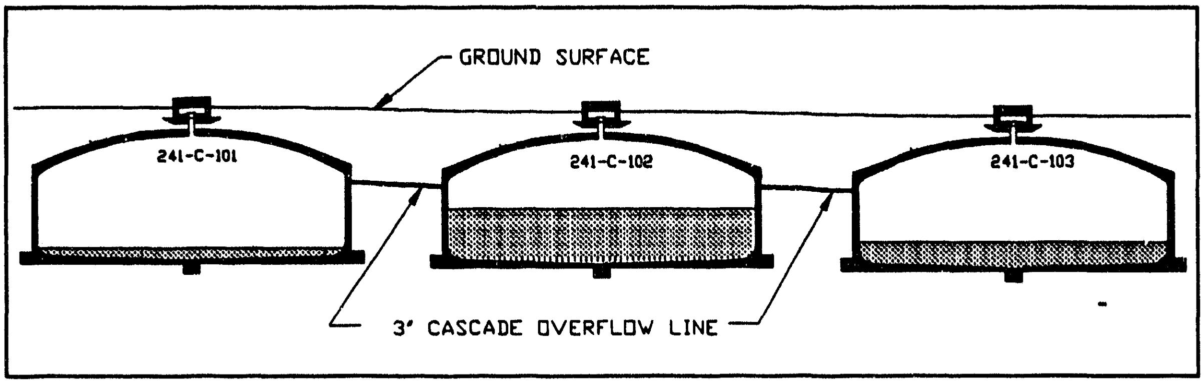


Figure 2-2. The Tank 241-C-101, 241-C-102, and 241-C-103 Cascade.



Evidence of headspace mixing was recently obtained during the December 1993 vapor sampling event in tank 241-C-103. Resistance temperature devices (RTDs) located on the sampling line indicated that the headspace temperature was 40 °C about 0.9 m (3 ft) above the surface and also at a point 3.05 m (10 ft) higher. This is consistent with the expectation that if convection is significant, the steepest temperature gradients would be found in the relatively stagnant regions very near the surface and near the dome, and that a relatively small temperature gradient would exist between those regions.

Visual inspection through the observation riser during the December sampling event was performed shortly after the cover flange was removed, and indicated that a low particle number density, non-uniform aerosol did exist in the riser itself. The thermal gradient between the cool riser cover flange and the tank headspace itself was apparently large enough to promote convection within the 4.9-m (16-ft)-long, 30.5-cm (12-in.)-diameter riser, producing an aerosol as warm, moist tank air contacted air cooled by the riser flange. This observation suggests that even air within the risers is not subject to stagnation as long as the top of the riser is occasionally much cooler than the headspace.

2.3 HEADSPACE BREATHING

Pressure differences between the atmosphere and tanks 241-C-101, 241-C-102, and 241-C-103 due to generation of gases and vapors in the tanks and to barometric changes, are relieved by passive ventilation. Each tank has a dedicated breather riser that is equipped with a high-efficiency particulate air (HEPA) filter to limit release of radioactive particulates from the tank. Additionally, small openings and cracks in the pit covers and unsealed risers allow some air to pass unfiltered between the tanks and the atmosphere.[1] Currently, valves at the HEPA filters of tanks 241-C-101 and 241-C-103 are shut, so that all 3 tanks in the cascade breathe through tank 241-C-102 and its HEPA filter. This has been the ventilation configuration since March 1993.

Changes in the barometric pressure cause passively ventilated storage tanks at the Hanford Site to exchange an average of 0.46 percent of the air in their headspaces with the atmosphere per day[2]. Given the headspace volume of tank 241-C-103 is about 2,550 m^3 (90,000 ft^3), barometric pressure changes would cause about 11.6 m^3 (410 ft^3) of air to be exchanged between the tank and the atmosphere each day. During an average day, the barometric pressure rises for approximately 8 hours, falls for approximately 8 hours, and shows negligible changes during the remaining 8 hours (Crippen 1993).

Dry instrument air is also introduced at a rate of 1.4 to 1.7 m^3/hr (50 to 60 ft^3/hr) at the FIC level gauge housing of tanks 241-C-102 and 241-C-103 to prevent condensation of moisture in the housing[3]. This flow rate of instrument air results in about 1.3 to 1.7 percent of the headspace being purged each day. The typical diurnal barometric cycle is such that some air would still be drawn into tank 241-C-103 from tank 241-C-102 and from unsealed risers and pit covers, but only during the steepest barometric pressure increases. In summary, the average total daily inflow of fresh air is estimated to be no more than about 2 percent of the headspace volume.

2.4 HEADSPACE TEMPERATURE

The waste and headspace temperatures are monitored on a weekly basis. Three thermocouples are located in the waste; the lowest thermocouple is essentially on the tank bottom, the second 0.61 m (2 ft) above the bottom, and the third 1.22 m (4 ft) above the bottom. The sole thermocouple in the headspace is approximately 2.79 m (9 ft 2 in.) above the waste surface.

The thermocouples in tank 241-C-103 indicate the waste and headspace temperatures fluctuate with the seasons, and are generally hottest in October and November, and coolest in

---

[1] The potential spread of radioactive contamination via these pathways is monitored by area air monitors, and is being addressed by the EPA (Pelletier 1993).

[2] This value was calculated in the manner of Garfield 1975, using hourly barometric readings for 1988, 1989, 1990, and 1991 from Crippen 1993, and assuming negligible resistance to the exchange of air.

[3] The rotameters on tanks 241-C-102 and 241-C-103 measuring flow of instrument air were monitored on several occasions during November and December 1993. Air flow was observed to fluctuate in the stated range, apparently due to minor supply pressure fluctuations.

April and May. These seasonal changes are related to ground temperatures (Crowe et al. 1993). Given the relatively small fraction of headspace gases exchanged per day as discussed in Section 2.3, effects on the temperature of the headspace by the diurnal inflow of cold or hot ambient air appear to be negligible. The headspace temperature of tank 241-C-103 has been observed to be as high as 44 °C (111 °F) and as low as 37 °C (98.6 °F) in the last two years.

Gradual reduction of the heat-generating radioactive materials in the waste tanks by radioactive decay results in successively less heat generation and cooler waste temperatures. Recent thermocouple data indicate that tank 241-C-103 is cooling at a rate of about 0.6 °C (33 °F) per year (Crowe et al. 1993). The radiolytic and chemical production of flammable gases and vapors by first order reaction kinetics should also decline. Furthermore, as the tank cools, the vapor pressure of the organic liquid in the tank will also decrease.

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3.0 FLAMMABLE HEADSPACE CONSTITUENTS AND THEIR MEASUREMENT

The flammability of a mixture of gases and vapors depends on the concentrations of fuel and an oxidizer. In the headspace of tank 241-C-103, the only significant oxidizer known to be present is oxygen[4], which is at roughly the same concentration as it is in normal air. Fuels known to be present in the headspace of the tank include inorganic gases such as ammonia and hydrogen, organic gases such as methane, volatile organic vapors such as acetone and butanol, and semivolatile organic vapors such as NPH and TBP (Ulbricht 1991, WHC 1993, Ligotke et al. 1994, and Einfeld 1994).

3.1 COMBUSTIBLE GAS METERS

Combustible gas meters (CGMs) are used routinely by health and safety technicians at the Hanford Site to assess the flammability of waste tank gases and vapors prior to intrusive tank work. CGMs provide a digital readout of the fuel content of an air sample as a percentage of the lowest concentration of fuel which will support flame propagation, the lower flammability limit (LFL). When calibrated with pentane, as has been determined to be optimal by WHC Industrial Hygiene Field Services, the CGMs tend to overestimate the contributions of such combustible gases as hydrogen and methane to the flammability of a sample (ISC 1991). Conversely, the CGMs used tend to underestimate the fuel value of high molecular weight organic vapors. An important example of the latter is NPH, for which a pentane-calibrated CGM may underestimate the fuel value by as much as a factor of 3 (Estey 1992).

Monitoring of the November and December sampling events was performed using an Industrial Scientific Corporation model TMX-410 meter. It was calibrated with pentane each morning prior to use, according to a standard single-point calibration method per the manufacturer's specifications. According to the CGM, total fuel content was determined to be 0 to 7 percent of the LFL from a total of 11 readings at risers #2, #7, and #8 (WHC 1993). Three readings of the headspace, taken via a tube lowered through riser #7 into the headspace approximately 4.9 m (16 ft) above the waste surface on December 2, 14, and 15, were 4, 7, and 7 percent of the LFL, respectively. A similar reading of the headspace, taken just prior to sample probe installation in riser #7 on January 21, 1994, was 6 percent of the LFL.

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[4] Sample analyses indicate nitrogen oxides, organic nitrates, and certain other oxidizers are not present at concentrations high enough to affect the headspace flammability (e.g., Einfeld 1994).

3.2 FLAMMABLE GASES

Flammable gases such as hydrogen, methane, and ammonia are known to be produced by radiolytic and chemical reactions within the high-level waste. As such, their current levels reflect a dynamic balance between their generation rates and such depletion mechanisms as tank breathing.

Hydrogen and methane have been detected in tank 241-C-103. Air samples collected in November from the FIC riser (#8) and the HEPA filter riser (#2) were analyzed and determined to contain between 590 and 874 parts per million by volume (ppm) hydrogen, and between 13.2 and 17.7 ppm of methane (Einfeld 1994). Given that the LFL for hydrogen is 4.0 percent by volume, and 5.0 percent by volume for methane (Zabetakis 1965), these air samples contained between 1.5 and 2.2 percent of the hydrogen LFL, and between 0.03 and 0.04 percent of the methane LFL.

The concentration of ammonia is not expected to be near its LFL of 15 percent by volume (Zabetakis 1965). Though validated sampling for ammonia in tank 241-C-103 has not been conducted, industrial hygiene monitoring during the November and December sampling events indicated a maximum ammonia concentration of 200 ppm. This corresponds to 0.13 percent of the LFL for ammonia.

The CGM monitoring data supports the argument that these permanent gases are not present at levels of concern. Since the CGM used during the November and December 1993 sampling events overreacts to the presence of hydrogen by about a factor of 2 (ISC 1991), the hydrogen in the headspace would account for roughly half of the 4 to 7 percent of the LFL response of the CGM.

3.3 FLAMMABLE ORGANIC VAPORS

The flammable organic compounds in the headspace of tank 241-C-103 may be classified as being either semivolatile or volatile. The semivolatile organic compounds present in the headspace come primarily from evaporation of the organic liquid waste. The dominant species in the organic liquid, namely TBP, n-$C_{12}H_{26}$, n-$C_{13}H_{28}$, and n-$C_{14}H_{30}$, are all found in the vapor phase. The volatile organic compounds present in the headspace are primarily radiolytic or chemical degradation products of semivolatile and nonvolatile organic waste.

The December 1993 vapor sampling event was performed to quantify the NPH and TBP present in the headspace of tank 241-C-103. Headspace samples were collected using OSHA versatile sampler (OVS) traps, which were lowered through the observation riser (#7) to an elevation about 0.9 m (3 ft) above the waste surface. OVS traps contain a prefilter to trap and coalesce any aerosol droplets, and two layers of a solid sorbent that adsorb semivolatile organic vapors. Laboratory testing of the OVS traps, including aerosol challenge testing and extraction efficiency testing, as well as analytical quantitation methodology, has been documented by Ligotke et al. (1993). A total of 10 OVS trap samples were collected from the headspace, with one being sacrificed for a radiolytic assay to allow transport of samples to the laboratory. The design of the OVS traps, sampling equipment, and detailed analyses results are discussed by Ligotke et al. (1994).

NPH quantitation results from the December vapor sampling are summarized in Table 3-1. Uncertainties in the values reported were estimated to be 21 percent by Ligotke et al. (1994), the dominant uncertainty being 20 percent due to analytical quantitation. Total sample volumes for OVS 1, 2, and 3 were about 0.22 L; volumes for OVS 4, 5, and 6 were about 0.88 L; and volumes for OVS 8, 9, and 10 were about 4.4 L. Comparison of values in the last column of Table 3-1 suggests the discrepancies between samples are related to the volumes of air sampled. Though no reason for this apparent relationship has been established, it may be due to the specific manner in which NPH was extracted from the three sets of OVS traps.

Table 3-1. NPH Concentrations Measured in OVS Traps from Tank 241-C-103.

Sample number	n-$C_{11}H_{24}$ mg/L	n-$C_{12}H_{26}$ mg/L	n-$C_{13}H_{28}$ mg/L	n-$C_{14}H_{30}$ mg/L	n-$C_{15}H_{32}$ mg/L	Total NPH mg/L
OVS 1	<0.07	0.306	0.429	0.100	<0.07	0.835
OVS 2	<0.07	0.287	0.435	0.085	<0.07	0.807
OVS 3	<0.07	0.247	0.336	0.076	<0.07	0.659
OVS 4	<0.02	0.278	0.401	0.103	<0.02	0.782
OVS 5	<0.02	0.235	0.358	0.099	<0.02	0.692
OVS 6	<0.02	0.215	0.349	0.058	<0.02	0.622
OVS 8	<0.003	0.411	0.527	0.129	<0.003	1.067
OVS 9	<0.003	0.383	0.574	0.158	<0.003	1.115
OVS 10	<0.003	0.349	0.578	0.140	<0.003	1.067
Average	-	0.301	0.443	0.105	-	0.850

As indicated in Table 3-1, quantities of n-$C_{11}H_{24}$ and n-$C_{15}H_{32}$ were below limits of detection in all samples. n-$C_{11}H_{24}$, typically present in significant quantities in the PUREX process diluent, has apparently been virtually eliminated by preferential evaporation from the organic waste during 24 years of storage in the tank farm. The very low vapor pressure of n-$C_{15}H_{32}$, and its low concentration in the organic liquid waste, explain its absence at analytical detection levels.

In addition to the three dominant NPH species listed in Table 3-1, several other compoyunds were detected in the samples. These were neither positively identified nor quantitated, but initial screening indicated them to be semivolatile branched alkanes. Though quantitation by species was not attempted, NPH collectively represented about 90 percent of the total ion abundance of the mass spectra (Ligotke et al. 1994).

The headspace concentration of NPH indicated by averaging results from the nine samples is 0.85 mg/L, with an uncertainty of ± 0.18 mg/L. Given an LFL for NPH of approximately 46 mg/L (Zabetakis 1965), these results indicate the headspace to be at about 1.8 ± 0.4 percent of the LFL for NPH.

TBP was above the analytical detection limit only in OVS 8, 9, and 10. The maximum observed TBP concentration was about 0.05 mg/L, or roughly 4.3 ppm (Ligotke et al. 1994). Though TBP is properly considered a fuel, its vapor pressure is so low that the flashpoint of TBP-diluent mixtures is determined by the partial pressure of the diluent (Schulz et al. 1984). At the observed 0.05 mg/L concentration, TBP does not contribute significantly to the fuel content of the headspace.

Samples of the liquid organic waste in tank 241-C-103 were also collected during the December 1993 sampling event. Analysis indicates that the predominant components of the organic liquid waste are all semivolatile. The principle components of the organic liquid, listed approximately by increasing vapor pressures, are given in Table 3-2 (Pool and Bean 1994).

Liquid sample analyses support the vapor sample analyses; the three NPH species that dominate the vapor phase constitute over 80 percent of the non-phosphate species in the liquid phase. The partial pressure of alkanes is significantly reduced by the presence of TBP. While flashpoints of the alkanes listed in Table 3-2 range from 71 to 132 °C (159.8 to 269.6 °F), the flashpoint of organic liquid waste samples has been estimated to be in the vicinity of 100 °C (212 °F) (Pool and Bean 1994).

The introduction of fresh air to tank 241-C-103, either as dry instrument air or from the atmosphere by natural barometric changes, could reduce the concentration of flammable vapors. However, the breathing and instrument air purge rates are small relative to the headspace volume, so it is reasonable to expect the semivolatile organic vapors in the headspace to be nearly in equilibrium with the floating pool of organic liquid. Consequently, changes in the ventilation configuration, such as venting all three tanks of the cascade through tank 241-C-103, would not significantly impact the concentration of semivolatile organic vapors.

Table 3-2. Principle Constituents of Organic Liquid Waste in Tank 241-C-103.

Compound	Relative weight percent	Flashpoint[5] (°C)
n-dodecane (n-$C_{12}H_{26}$)	3.8	71
alkane*	0.3	
alkane*	1.5	
n-tridecane (n-$C_{13}H_{28}$)	15.5	79
alkane*	0.6	
alkane*	1.3	
n-tetradecane (n-$C_{14}H_{30}$)	8.1	99
alkane*	1.0	
n-pentadecane (n-$C_{15}H_{32}$)	1.2	132
dibutyl butyl phosphonate (DBBP)	2.6	
tributyl phosphate (TBP)	64.0	193

*Tentatively identified as branched alkanes in the $C_{12}H_{26}$ to $C_{14}H_{30}$ range.

Volatile organic compounds are not present in significant quantities in the organic liquid, according to the analysis shown in Table 2. Analyses of SUMMA®[6] canister vapor samples have indicated dozens of volatile organic compounds are present at trace quantities in the headspace, but definitive concentrations of these species are as yet unavailable (Einfeld et al. 1992, Einfeld 1994).

The contribution of volatile organic compounds to flammability of the headspace can be estimated from calibrated CGM data collected during the November and December 1993 sampling events. Assuming that the in-tank CGM readings of 7 percent of the LFL are correct, and that the CGM overcompensates for the hydrogen present by a factor of 2 (ISC 1991), and the response of the CGM to the NPH constituents is negligible, then volatile organic compounds would be responsible for 2.8 to 4.0 percent of the LFL as measured by the CGM.

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[5] Aldrich 1991

[6] SUMMA is a registered trademark of Molectrics, Inc., Cleveland, Ohio.

3.4 FLAMMABLE ORGANIC LIQUID AEROSOL

Aerosols form in the high-level waste tanks by the same mechanism as clouds form in the atmosphere. Warm, vapor-laden air from near the surface of the waste rises and is cooled below its dewpoint by contact with cool air from near the tank dome or the dome itself. While it may be said with reasonable confidence that an aerosol has existed in tank 241-C-103 in the past, it is not known whether the aerosol was composed of aqueous droplets, organic droplets or both (Huckaby and Estey 1992).

Inspections of this tank on December 2, 14, and 15, 1993 and January 21, 1994 indicated no visible aerosol was present in the headspace. That an aerosol did but presently does not exist in tank 241-C-103 may be due to a variety of effects, including the gradual cooling of the tank waste, reduction of the volatility of the organic layer, or seasonal temperature changes that result in an aerosol during certain times of the year but not others. Further consideration of an organic aerosol is given here because it cannot be proven yet that an organic aerosol does not exist at other times of the year. Planned sampling events will address this issue.

Key concepts for understanding the combustion of an aerosol of liquid NPH droplets have been given by Huckaby and Estey 1992. Essentially, the fuel available in the aerosol droplet phase must first be vaporized, and this consumes some of the energy of the fuel. Furthermore, droplets larger than about 1 μm in diameter are not apt to evaporate completely and thus burn before the rapidly moving flame front passes the droplet. This makes some of the fuel in larger droplets unavailable for flame propagation. These factors tend to increase the minimum concentration of fuel (vapor + aerosol) required for flame propagation in an aerosol-vapor system. Fuel in the aerosol droplet phase is less flammable than in the vapor phase. It is erring on the safe side to apply the calculated LFL for NPH vapor to an NPH aerosol-vapor system.

Estimates of the probable mass concentration of an NPH aerosol in tank 241-C-103 have been performed by Huckaby and Estey 1992 and Postma et al. 1994. The former estimated the concentration of the aerosol to be at or less than 1 mg/L from a report that the waste surface was visible through the aerosol, and from considerations of likely aerosol mass loading. Given an LFL for NPH of about 46 mg/L, this aerosol mass concentration would be about 2.2 percent of the LFL.

Postma et al. 1994 used the MAEROS-2 program (Gelbard 1982) to model the formation and deposition rate of an organic aerosol in the tank. Their simulation predicted a mass concentration of 0.043 mg/L. Allowing for possible errors in the estimation of conditions and properties, a worst-case calculation was run by increasing the aerosol generation rate by a factor of 10. The maximum aerosol mass concentration for this case was calculated to be 0.22 mg/L. These estimated and estimated maximum aerosol mass concentrations correspond to about 0.1 and 0.5 percent of the LFL for NPH, respectively.

In summary, though no aerosol was observed in the headspace of tank 241-C-103 in December 1993, it is possible that temperature changes promote the existence of an aerosol at other times of the year. If an organic liquid aerosol is produced at other times, calculations indicate that it would not contribute significantly to the flammability of the headspace.

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4.0 CONCLUSIONS

Data and evidence have been presented that indicate gases and vapors in the headspace of tank 241-C-103 are well below the LFL. The principle fuels in the headspace are thought to be: hydrogen, present at 1.5 to 2.2 percent of its LFL; the semivolatile NPH vapor, present at 1.4 to 2.2 percent of its LFL; and volatile organic vapors, collectively present at 2.6 to 4.0 percent of their LFL. Assuming the independence of these calculated flammability contributions, the flammability of the headspace is estimated to be between 5.5 and 8.4 percent of the LFL of the mixture. This is well within the operational guideline limit of 20 percent of the LFL established by Tank Farm Safety.

Recent inspections of the tank 241-C-103 headspace indicate that no visible aerosol is currently present. In the event that an aerosol is present under marginally different tank conditions, calculations discussed indicate that the mass concentration of NPH in the aerosol droplet phase would not significantly affect the headspace flammability. Additional sampling will be performed to verify the premise that the vapors do not change significantly with time or season.

Though the observed levels of hydrogen gas are greater than expected, the estimated fuel content of the tank 241-C-103 headspace is within bounds set by the engineering assessment of Huckaby and Estey 1992.

Further vapor sampling of tank 241-C-103 is being performed to address the issue of vapor toxicity. Analytical data from this sampling will be evaluated to reaffirm current understanding of the headspace flammability and to verify that seasonal changes in the headspace do not significantly alter this document's conclusions.

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5.0 REFERENCES

Aldrich Chemical Company, 1991, *Catalog Handbook of Fine Chemicals*, Aldrich Chemical Company, Milwaukee, Wisconsin.

Burke, T. M., 1991, *Summary of Evaporation Modeling for Tank 241-C-103*, (internal memorandum to R. E. Raymond, April 11), Westinghouse Hanford Company, Richland, Washington.

Carothers, K. G., 1988, *Tank 103-C Transaction History - Post January 1976*, (internal memorandum 13331-88-600 to D. A. Dodd, G. L. Dunford, G. N. Hanson, A. W. Lilly and R. E. Van der Cook, September 22), Westinghouse Hanford Company, Richland, Washington.

Conrad, R. B., 1993, *241-C-103 Vapor Phase Characterization*, WHC-SD-WM-WP-174, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Crippen, M. D., 1993, *Barometric Pressure Variations*, WHC-EP-0651, Westinghouse Hanford Company, Richland, Washington.

Crowe, R. D., M. Kummerer and A. K. Postma, 1993, *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures*, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington.

Einfeld, W. and L. Bustard (Sandia National Laboratories, Albuquerque, New Mexico) and R. A. Rasmussen (Oregon Graduate Institute of Science and Technology, Beaverton, Oregon), 1992, *Progress Report - Hanford Tank 103C Vapor Analysis: Evaluation of Canister Sampling and Analysis Techniques*, report prepared for J. W. Osborne, Westinghouse Hanford Company, Richland, Washington.

Einfeld, W., 1994, letter dated January 20 to J. W. Osborne, WHC, transmitting Sandia National Laboratories review draft contractor report SAND94-0229, R. A. Rasmussen, lead author, *Analysis of Headspace Vapor Samples Collected at Hanford Tank C-103*, November 1993, Sandia National Laboratories, Albuquerque, New Mexico.

Estey, S. D., 1992, *Flammability Issue Resolution for 241-C-103*, (internal memorandum 7K210-92-446 to M. H. Shannon, October 12), Westinghouse Hanford Company, Richland, Washington.

Garfield, J. S., 1975, *Anticipated Natural Air Breathing Rate for Underground Tanks*, ARH-CD-256, Atlantic Richfield Hanford Company, Richland, Washington.

Gelbard, F., 1982, *MAEROS User Manual*, NUREG/CR-1391, SAND80-0822, Sandia National Laboratories, Albuquerque, New Mexico.

Hanlon, B. M., 1994, *Tank Farm Surveillance and Waste Status Summary Report for September 1993*, WHC-EP-0182-66, Westinghouse Hanford Company, Richland, Washington.

Huckaby, J. L., 1993, *Engineering Work Plan for Aerosol and Vapor Sample Collection in Tank 241-C-103*, WHC-SD-WM-WP-198, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Huckaby, J. L. and S. D. Estey, 1992, *An Engineering Assessment of the Aerosol and Vapor Flammability in 241-C-103*, WHC-SD-WM-ER-181, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

ISC, 1991, *Cross Sensitivity Multipliers for CMX, HMX, MX250 and MX251 Combustible Detectors*, March 7, drawing 1703A1287-200, Industrial Scientific Corporation, Oakdale, Pennsylvania.

Ligotke, M. W., and T. R. Clauss, G. W. Dennis, S. C. Goheen, J. L. Huckaby and R. B. Lucke, 1993, *Aerosol and Vapor Characterization of Tank 241-C-103: Flammability Assessment Sampling System and Method Validation*, PNL-8875, Pacific Northwest Laboratory, Richland, Washington.

Ligotke, M. W. and T. R. Clauss, J. S. Fruchter, R. B. Lucke and S. C. Goheen, 1994, *Waste Tank Vapor Project - Aerosol and Vapor Characterization of Tank 241-C-103: Data Report for OVS Samples Obtained 12/02/93*, Pacific Northwest Laboratory, Richland, Washington.

Osborne, J. W., and J. L. Huckaby, T. P. Rudolph, E. R. Hewitt, D. D. Mahlum, J. Y. Young, and C. M. Anderson, *Tank 241-C-103 Vapor and Gas Sampling Data Quality Objectives*, WHC-EP-0774, Westinghouse Hanford Company, Richland, Washington.

Pelletier, R. F., 1993, *EPA Draft Report on Estimating Radionuclide Air Emissions from Diffuse and Fugitive Sources*, (internal memorandum to Distribution, July 28), U. S. Department of Energy, Washington, D.C.

Pool, K. H. and R. M. Bean, 1994, *Analysis of Liquid Samples from Hanford Waste Tank 241-C-103*, PNL-9403, Pacific Northwest Laboratory, Richland, Washington.

Postma, A. K., D. B. Bechtold, G. L. Borsheim, J. M. Grigsby, R. L. Guthrie, M. Kummerer, M. G. Plys, and D. A. Turner, 1994, *Safety Analysis of Exothermic Reaction Hazards Associated With the Organic Liquid Layer in Tank 241-C-103*, WHC-SD-WM-SARR-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Prentice, B. A., 1991, *Organic Analysis of 103-C Tank Samples (Westinghouse Work Order ED1150)*, (letter to R. K. Tranbarger, Westinghouse Hanford Company, Richland, Washington, April 11), Pacific Northwest Laboratory, Richland, Washington.

Schulz, W. W., J. D. Navratil, and A. E. Talbot, 1984, *Science and Technology of Tributyl Phophate, Volume I Synthesis, Properties, Reactions and Analysis*, CRC Press, Inc., Boca Raton, Florida.

Story, M. S., 1992, *Assessment of Waste Tank Vapor Cryogenic Sampling and Analysis*, (report prepared for Pacific Northwest Laboratory by Northwest Instrument Systems, Inc., Kennewick, Washington, May 22).

Trent, G. J., 1990, *Draft Report: Characterization Study of the Headspace Gases in Tanks 102-C and 103-C*, Westinghouse Hanford Company, Richland, Washington.

Ulbricht, W. H. Jr., 1991, *Report on 241-C Tank Farm Air Sampling Results of 1989*, WHC-SD-WM-RPT-019, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

van Tuyl, H. H., 1983, *Safety of Organic Solvents in Waste Tanks*, (letter 083083 to W. V. Baumgartner, Westinghouse Hanford Company, Richland, Washington, August 30, 1983), Pacific Northwest Laboratory, Richland, Washington.

WHC, 1993, Industrial Hygiene Monitoring Reports for: 11/11/93, 11/12/93, 11/15/93 and 11/16/93 (Work Packages 2E-92-1564/W and 2E-93-0128/W); 12/02/93 (Work Package 2E-92-01760/W); 12/14/93 (Work Package 2E-92-01760/2); and 12/15/93 (Work Package 2E-92-01760/2), Westinghouse Hanford Company, Richland, Washington.

Wood, S. A., 1992, *Gas Space Analysis for Tank 241-C-109*, WHC-SD-WM-ER-183, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Zabetakis, M. G., 1965, *Flammability Characteristics of Combustible Gases and Vapors*, U. S. Department of the Interior, Bureau of Mines, Washington, D.C.

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