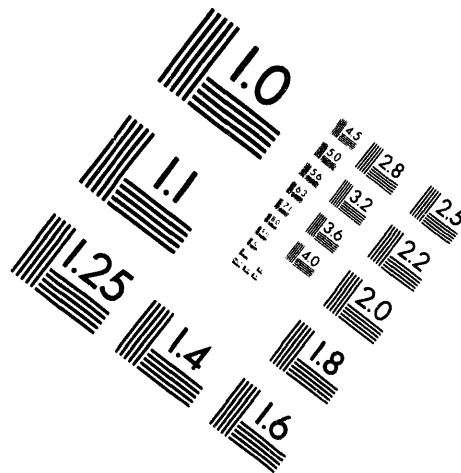
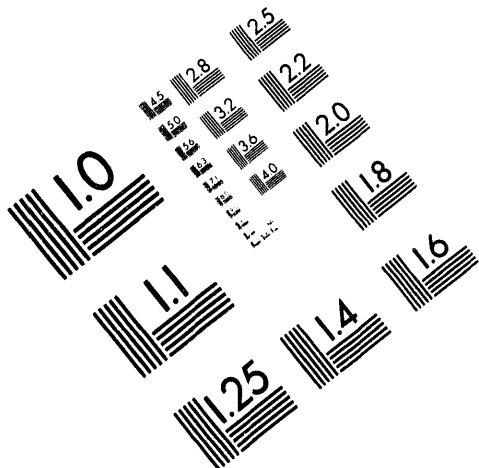




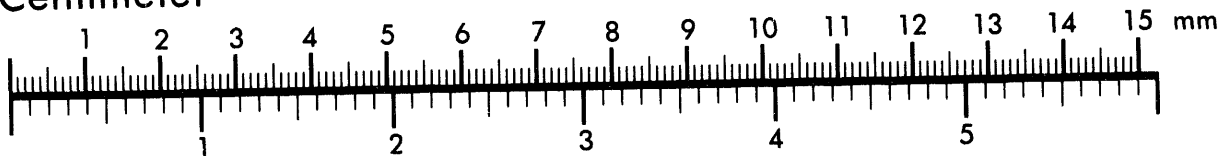
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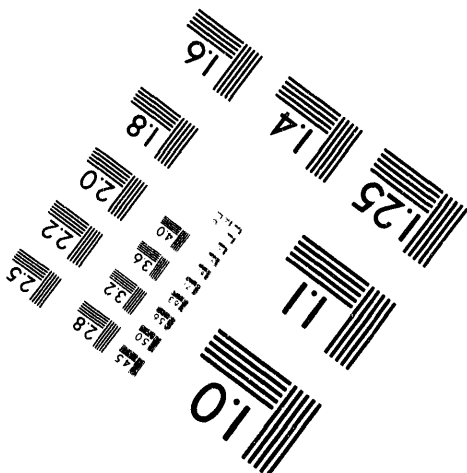
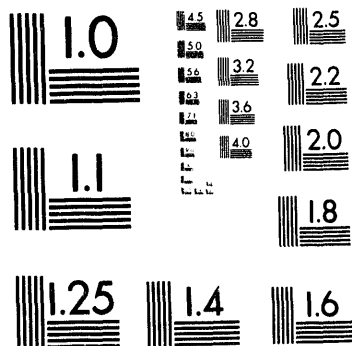
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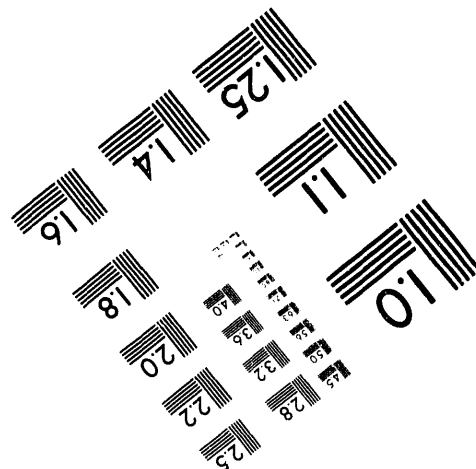
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Revision 0

Safety Analysis of Exothermic Reaction Hazards Associated With the Organic Liquid Layer in Tank 241-C-103

A. K. Postma
D. B. Bechtold
G. L. Borsheim
J. M. Grigsby
R. L. Guthrie
M. Kummerer
M. G. Plys*
D. A. Turner

March 1994

*Fauske and Associates

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Office of Environmental Restoration and
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Westinghouse
Hanford Company Richland, Washington

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LIST OF TERMS

AIT	Autoignition temperatures
CGM	Combustible gas meter
DOE	U.S. Department of Energy
EDTA	Ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
FAI	Fauske and Associates
FIC	Food Instrument Company
FTIR	Fourier Transformed InfraRed
GCMS	Gas Chromatographic/Mass Spectrometry
HEPA	High-efficiency particulate air
HPT	Health Physics Technician
ISB	Interim safety basis document
JCO	Justification for continued operations
LFL	Lower flammable limit
LOW	Liquid observation well
NPH	Normal paraffin hydrocarbons
OVS	Occupational Safety and Health Administration (OSHA) Versatile sampler
PNL	Pacific Northwest Laboratory
PUREX	Plutonium-Uranium Extraction Plant
TBP	Tributyl phosphate
TBP-NPH	Tributyl phosphate and normal paraffin hydrocarbons
TCT	Thermocouple tree
TOC	Total organic carbon
USQ	Unreviewed Safety Question
WHC	Westinghouse Hanford Company

1.0 SUMMARY AND CONCLUSIONS

1.1 SUMMARY

This report identifies and evaluates safety hazards associated with the interim storage of a potentially flammable organic liquid in the 241-C farm waste tank C-103. The objective of this study is to provide a technical basis for closing the unreviewed safety question (USQ) that was declared in 1992 (Grantham 1992). A USQ was determined to exist because potential reactions associated with the floating organic layer had not been adequately addressed in the existing safety analysis report (Bergmann 1986).

The potential hazards of uncontrolled exothermic chemical reactions during interim storage of the organic liquid in tank C-103 were identified as the following: (1) a deflagration in tank headspace air, (2) a pool fire at the air/organic liquid interface, and (3) organic-nitrate/nitrite reactions in liquid and solid wastes. These three hazards were evaluated to identify conditions under which significant reaction could occur. Comparing tank conditions with those necessary for a significant uncontrolled reaction permitted the risk posed by the hazards to be evaluated.

Current tank conditions and key waste properties were determined from a study of tank data and data obtained from the analysis of waste samples taken from this tank. Tank operations associated with continued storage of waste in tank C-103 were evaluated against the hazards to identify potentially credible accident sequences. Controls and monitoring needed to assure that uncontrolled exothermic reactions do not occur during interim storage were identified.

The key finding of this study is that uncontrolled exothermic reactions can be prevented by imposing minimal controls and monitoring requirements. The occurrence of a pool fire can be precluded by preventing the introduction of energetic ignition sources. A deflagration in headspace air can be prevented by maintaining the concentration of combustible species below the lower flammability limit (LFL). Organic-nitrate/nitrite reactions do not pose a significant hazard because reactant concentrations are too low to yield significant energy.

1.2 CONCLUSIONS

Specific conclusions and summary statements that are supported by this study are listed as follows.

1. The floating organic liquid in tank C-103 is primarily normal paraffinic hydrocarbons (NPH) and tributyl phosphate (TBP). The measured flashpoint of this liquid is 118 ± 2 °C, so it would not support a pool fire unless heated (locally) appreciably from its current temperature of 40 ± 4 °C. Because its

flashpoint is higher than 93.3 °C (200 °F) the organic liquid ranks in the least-flammable class (Class III B) of combustible liquids classified by the National Fire Protection Association.

2. Decay heat currently is removed by the passive means of conduction in the waste and surrounding soil and by convection and radiation in the headspace air. No active systems exist that could fail and thereby cause significant waste heatup.
3. Controls on tank operations that are needed to preclude a pool fire include a means to prevent gasoline spills from vehicles, and operational controls to prevent the introduction of flaming objects or heaters that could initiate a pool fire.
4. Recent sample results provides assurance that the concentration of combustible species in headspace air (gases and aerosols) is well below the 25% LFL criterion suggested for this tank. The concentrations of organic gases, vapors, and aerosols sum to approximately 5% LFL. Hydrogen and ammonia add another 2% LFL for a total of approximately 7% LFL.
5. The concentration of combustible species in headspace air of radiolytic origin is dependent on the ventilation rate (induced by atmospheric pressure fluctuation, instrument purge air, and natural convection) of the headspace air. The concentrations of organic species that volatilize from the organic liquid, on the other hand, are expected to remain constant and close to the saturation value, independent of ventilation rate.
6. Controls and monitoring needed to maintain combustible species below 25% LFL are:
 1. Semiannual measurements of combustible gases in headspace air, or
 2. Venting of tank C-103 directly to the atmosphere through its own filtered vent along with annual measurements of combustible gases in headspace air.
7. Adiabatic calorimetry test results and analytical measurements of nitrated alkane concentrations performed on samples of the organic liquid provide evidence that exothermic reactions in the liquid phase would yield too little energy to represent a safety hazard. Calculations based on organic carbon concentration: measured in samples of aqueous supernatant liquid and in sludge samples show that potential exotherms are too small for organic-nitrate/nitrite to pose a safety hazard in either the sludge or overlying supernatant liquid.

2.0 OBJECTIVE AND SCOPE

2.1 OBJECTIVES

This study evaluates exothermic reaction hazards associated with a floating layer of organic liquid in tank C-103. Results of the study are to provide a technical basis for closing the USQ that now exists and to identify controls and monitoring needed to avoid an accident caused by the presence of the organic liquid.

2.2 SCOPE

This study focuses on flammability and runaway chemical reaction hazards caused by the presence of the organic liquid in tank C-103. Tank operations considered are those expected to be carried out during interim storage (i.e., the time period before removal of the organic liquid). Current plans (Fulton 1993) call for the removal of the organic liquid by March 1995. Because the methods to be used to remove the liquid are not yet well defined, hazards involved in the removal operation are not considered herein. Potential toxicological hazards associated with tank C-103 are under study in a separate work effort (Osborne 1992) and are not considered in this report.

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3.0 BACKGROUND

3.1 OVERVIEW OF TANK C-103

Tank C-103 is on a Watch List at the Hanford Site because it contains a floating organic liquid layer (Hanlon 1993). Unevaluated reaction hazards posed by the presence of the organic liquid were determined to be a USQ (Grantham 1992) for this tank. This tank was placed on the Watch List because of the USQ.

Tank C-103 is one of twelve 22.9 m (75 ft) diameter tanks having nominal capacities of 2010 m³ (530,000 gal) in C Tank Farm located in the 200 East Area. This tank is third in a three-tank cascade; its floor is 0.31 m (1 ft) lower than the upstream tank C-102. The tank is buried; the center of its dome-shaped top is covered by approximately 2.7 m (9 ft) of earth.

The waste in tank C-103 is composed of a bottom layer of sludge, a middle layer of aqueous supernatant liquid, and a relatively thin top layer of organic liquid. Sludge depth, referenced to the bottom center of the tank averages 1.2 m (49 in.) in depth. The total depth of sludge plus supernatant liquid amounts to 2 m (78 in.). Waste depth in this tank is low compared to a design depth of 5 m (16 ft) for a full tank.

3.2 ORGANIC LIQUID LAYER

An organic liquid, immiscible with water, floats on the aqueous supernatant liquid in tank C-103. The organic liquid was transferred into tank C-103 from tanks C-102 and C-104 in 1975 (Hopkins 1992). The liquid, a mixture NPH and TBP, is thought to have originated from the Plutonium-Uranium Extraction (PUREX) separation plant. The PUREX process used an organic liquid, composed of 30% TBP and 70% NPH on a volumetric basis, as an extractant. Partial evaporation of the organic liquid during periods of forced ventilation of tank C-103 between 1975 and 1992 has reduced the volume of the liquid and depleted the more volatile hydrocarbons that were initially present in the NPH.

3.3 DETERMINATION OF UNREVIEWED SAFETY QUESTION

During 1992, the safety of continued storage of the floating organic liquid in tank C-103 was reviewed by Westinghouse Hanford Company (WHC). As a result of the review, the storage

of the potentially flammable liquid in tank C-103 was determined to be a USQ* (Grantham 1992). Several actions are triggered by the USQ determination.

- Operations at the facility are restricted to those deemed to be necessary for safe operation.
- A justification for continued operations (JCO) is prepared to identify operations allowed and the basis for why the allowed operations do not pose an unacceptable hazard in light of the USQ designation. A JCO has been prepared for tank C-103 (Carothers 1993).
- A safety review of the facility/operation is prepared to determine what hazards exist and their potential consequences. Based on the findings of the safety review, a judgment will be made that: (1) the hazards fall within currently defined safety envelopes, (2) the larger safety envelopes apply and are acceptable, or (3) a mitigation effort is required to reduce the potential risk posed.

This report documents the safety review process identified above.

3.4 POTENTIAL HAZARDS OF INTERIM STORAGE

Potential hazards of interim storage of organic liquid in tank C-103, as identified in the Interim Safety Basis (ISB) document (Leach and Stahl 1993a) are described as follows.

3.4.1 Deflagration in Headspace Air

A hypothetical sequence of events that describes this postulated hazard is as follows.

*The USQ designation is a formal procedure required under specific orders from DOE (DOE 1986; DOE 1991). The USQ orders state, "A proposed change, test or experiment shall be deemed to involve an unreviewed safety question if:

- The probability of occurrence or the consequences of an accident or malfunction of equipment important to safety, evaluated previously by safety analysis will be significantly increased, or
 - A possibility for an accident or malfunction of a different type than any evaluated previously by safety analysis will be created which could result in significant safety consequences."
-
-

- Combustible species originating from radiolysis, from the evaporation of volatile components of the liquid, from the formation of organic mists, or other processes build in headspace air to flammable concentrations.
- An ignition source is accidentally introduced into the flammable air-fuel mixture and the mixture is ignited.
- Combustion in headspace air causes a temperature and pressure increase that results in a pressurized release of combusted gases and entrained material to the atmosphere. Relatively low developed pressures [(~ 7 kPa (1 lb/in²))] could rupture high-efficiency particulate air (HEPA) filters. Tank structural integrity would be challenged for higher combustion pressures.

The deflagration event described above is impossible if the combustible species concentrations are lower than the LFL.

3.4.2 Combustion of Organic Liquid as a Pool Fire

A hypothetical sequence of events that describes this postulated hazard is as follows.

- The floating liquid is assumed to be flammable (i.e., will support a flame if ignited locally).
- The liquid is ignited locally, and flame spreads over a large area of the pool.
- The pool fire causes pressure and temperature to rise in headspace air. If sufficiently high pressures are reached, then a pressurized release of combusted gases and entrained material to the atmosphere could take place. Relatively low developed pressure [(~ 7 kPa (1 lb/in²))] could rupture HEPA filters. Tank structural integrity would be challenged for higher combustion pressures.

Initiating a pool fire over a liquid that is highly subcooled compared to the flashpoint requires that the liquid be heated (at least locally) to above the flashpoint and the introduction of an ignition source into a flammable air-fuel mixture above the pool.

3.4.3 Organic-Nitrate/Nitrite Reactions

Organic-nitrate/nitrite reactions are theoretically possible in both the organic liquid and in the sludge layer. A hypothetical sequence of events that describes the postulated hazard of organic-nitrate/nitrite reactions in the organic liquid is as follows.

- It is postulated that the TBP present in the organic liquid has reacted with nitrates and nitrites in the aqueous supernatant liquid on which the organic floats. An appreciable concentration of nitrated organics is thus postulated to have formed and to remain suspended in the organic layer.
- The organic liquid is heated to a reaction threshold temperature by means of a pool fire or other accident. An exothermic organic-nitrate/nitrite reaction occurs, resulting in the release of gases and thermal energy to the headspace air.
- Released gases and energy would cause an increase in tank pressure and could cause a release of headspace air and entrained material to the atmosphere. Relatively low developed pressures (~7 kPa [1 lb/in²]) could rupture HEPA filters. Tank structural integrity would be challenged for higher combustion pressures.

The scenario described above is possible only if exothermic reactions in the liquid release enough energy to rapidly generate gases.

A hypothetical sequence of events that describes the postulated hazard of organic-nitrate/nitrite reactions in sludge is as follows.

- Aqueous supernatant is assumed to be lost from the tank by a leak or pumping process, allowing the organic liquid to float on the sludge.
- The organic liquid is assumed to be flammable.
- An energetic ignition source is accidentally introduced into the tank at the pool air interface, igniting a pool fire. The pool fire spreads with time over a large area.
- Heatup of the sludge by the burning pool to the reaction onset temperature triggers a propagating organic-nitrate reaction in the sludge, leading to the release of heat and gases. Vented gases would carry entrained material, causing the release of radioactive material. Relatively low developed pressures (~7 kPa [1 lb/in²]) could rupture HEPA filters. Tank structural integrity would be challenged for higher combustion pressures.

The scenario described above is possible only if exothermic reactions in sludge release enough thermal energy to support a propagating reaction.

3.5 INFORMATION AVAILABLE TO CHARACTERIZE HAZARDS

3.5.1 Organic Liquid

Samples of the floating organic liquid, taken in December 1993 have been analyzed to characterize flammability and exothermic reaction hazards. Available data, detailed in Section 5.0, include the following:

- Layer thickness
- Chemical composition
- Flashpoint
- Organic-nitrate/nitrite reaction exotherms.

3.5.2 Combustibles in Headspace Air

A recent sampling effort has been conducted to quantify combustible species in headspace air. Concentration data, detailed in Section 5.0, are available for combustible species in the following categories.

- Sum of semivolatile organics (alkanes, TBP) and organic aerosols
- Gases (H₂, NH₃, CH₄, CO)
- Total nonmethane organics
- Total combustible species

3.5.3 Sludge and Aqueous Supernatant Liquid

Information on sludge composition is available from two core samples taken in 1986 (Weiss and Schull 1988). The chemical composition of the aqueous supernatant liquid is known from analyses performed on samples taken in 1991 (Edrington 1991) and in 1993 (Pool and Bean 1994). Pertinent information on sludge and aqueous supernatant liquid is presented in Section 5.0.

3.6 NATIONAL FIRE CODES FOR STORAGE OF FLAMMABLE AND COMBUSTIBLE LIQUIDS

Storage requirements specified in the National Fire Codes (NFPA 1986, 1990, 1991) are briefly reviewed here to help put the hazards posed by the organic liquid into perspective. While NFPA Codes do not address hazards posed by radioactive materials, and therefore are not adequate to provide a safety basis for tank C-103, the Codes help characterize the flammability hazard.

3.6.1 Classification of Flammable and Combustible Liquids

Liquids are classified as flammable or combustible on the basis of their flashpoints and vapor pressures. The breakdown of liquids into three major classes (Class I, Class II, and Class III) and five subclasses (IA, IB, IC, IIIA, IIIB) is summarized in Table 3-1. The classification scheme ranks liquids in terms of flammability hazard: Class IA is generally the most hazardous while Class IIIB is least hazardous.

The organic liquid in tank C-103 has a flashpoint greater than 200 °F (93.3 °C) (see Section 5.1) and is therefore classified as Class IIIB, the least hazardous class in NFPA 321.

3.6.2 Classification of Hazardous Locations for Electrical Installations

Two safety questions are posed in NFPA 497A for evaluating whether an area needs to be assigned a hazard classification.

1. Are flammable liquids or flammable gases likely to be present?
2. Are combustible liquids likely to be handled, processed, or stored at temperatures above their flashpoints?

The answer to both questions is "no" when the organic liquid alone is considered. On this basis, the presence of the organic liquid would not cause an area to be "classified" in terms of NFPA 497A.

3.6.3 Specific Requirements

Three specific requirements cited by NFPA Codes that appear to have applicability to tank C-103 are the following.

1. **Venting.** For underground tanks storing Class III liquids, vent pipes shall not be manifolded with vent pipes from tanks storing Class I liquids unless positive means are provided to prevent the vapors from Class I liquids from entering the tank, to prevent contamination and possible change in classification of the less volatile liquid. This requirement is specified in Section 2-4.5.5 of NFPA 30.
2. **Electrical Equipment.** Quoting from Section 2-3.5.3 of NFPA 497A, "Class IIIB liquids have flashpoints at or above 200 °F (93.3 °C). These liquids seldom evolve enough vapors to form ignitable mixtures even when heated and are seldom ignited by properly installed and maintained general purpose electrical equipment." Based on this statement, no special electrical installation requirements are needed for safe storage of the organic liquid in tank C-103.

Table 3-1. NFPA Classification of Flammable and Combustible Liquids (NFPA 1991).

Liquid class	Liquid properties
Class I - Flammable	Flashpoint ^a less than 100 °F (37.8 °C) and Reid vapor pressure ^b equal to or less than 40 psia (276 k Pa) at 100 °F (37.8 °C)
Subclass IA	Flashpoint less than 73 °F (22.8 °C) and boiling point less than 100 °F (37.8 °C)
Subclass IB	Flashpoint less than 73 °F (22.8 °C) and boiling point equal to or greater than 100 °F (37.8 °C)
Subclass IC	Flashpoint equal to or greater than 73 °F (22.8 °C) and less than 100 °F (37.8 °C)
Class II - Combustible	Flashpoint equal to or greater than 100 °F (37.8 °C) and less than 140 °F (60 °C)
Class III - Combustible	Flashpoint equal to or greater than 140 °F (60 °C)
Subclass III A	Flashpoint equal to or greater than 140 °F (60 °C) and less than 200 °F (93.3 °C)
Subclass III B	Flashpoint equal to or greater than 200 °F (93.3 °C)

^aClosed cup flashpoint

^bAs determined by ASTM D 323, Standard Method of Test for Vapor Pressure of Petroleum Products (Reid Method)

3. **Adequate Ventilation.** Quoting Section 2-6.2 of NFPA 497A, "Adequate ventilation is defined by NFPA 30, Flammable and Combustible Liquids Code, as that which is sufficient to prevent accumulation of significant quantities of vapor-air mixtures in concentrations over 25% of the lower flammable limit." This requirement is met in the headspace of tank C-103 because equilibrium vapor concentrations at the current storage temperature are below 25% of the LFL (see Section 5.6).

3.6.4 Summary of NFPA Code Requirements for Storage of Organic Liquid in Tank C-103

NFPA ranking of the organic liquid in tank C-103 puts it in the least hazardous class, Class IIIB. For Class IIIB liquid, few requirements beyond sound engineering practice are identified, and current storage conditions appear to meet NFPA Codes for flammable and combustible liquids. When judged from a liquid flammability standpoint, the organic liquid in tank C-103 poses a minimal hazard.

4.0 DESCRIPTION OF TANK C-103

4.1 PHYSICAL DESCRIPTION OF TANK

Tank C-103 is a 2010 m³ (530,000 gal) single-shell tank located in C Tank Farm in the 200 East Area. It was built in 1944 and first received waste in 1946. The tank is underground with a soil cover of approximately 2.7 m (9 ft) at the center of its dome-shaped roof. The tank is constructed of reinforced concrete and is lined on its floor and sidewall with 6.35 mm (1/4 in.) steel sheet. A cross-sectional elevation view of the tank and waste is shown in Figure 4-1. The tank is 22.9 m (75 ft) in internal diameter. Height varies from 6.1 m (20 ft) at the top of the cylindrical section to approximately 9.15 m (30 ft) at the center of the dome. The bottom of the tank is dished; the center is 0.3 m (1 ft) lower than the bottom near the vertical walls of the tank. The volume of the dished bottom is estimated to be 47.3 m³ (12,500 gal) (Hanlon 1993).

4.2 OPERATIONAL COMPONENTS

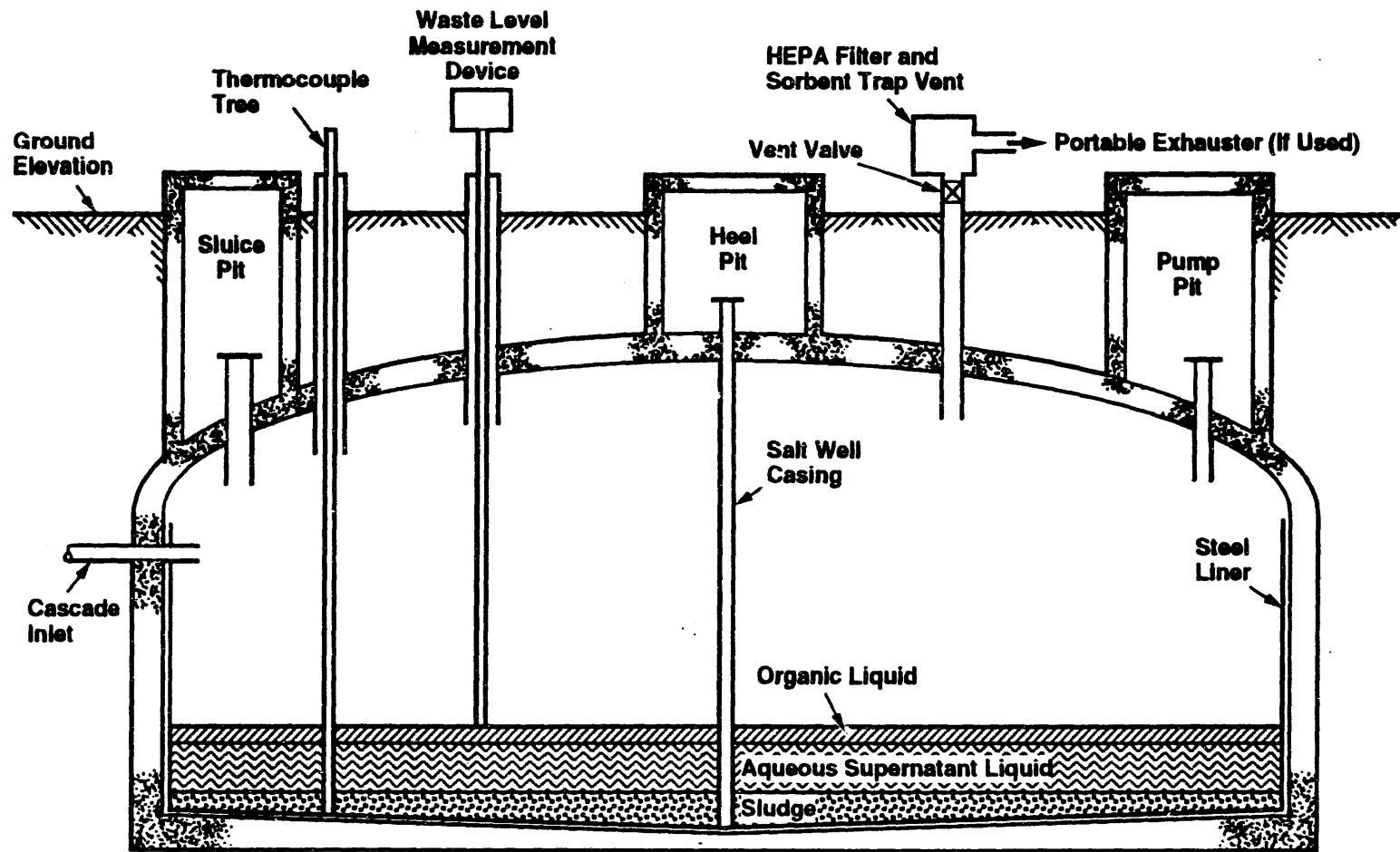
Operational components that may be used for waste transfer, monitoring, and control are described as follows.

4.2.1 Access Pits

Three access pits are shown schematically in Figure 4-1. From left to right they are sluice pit, heel pit, and pump pit. These pits provide access to the top of the tank and enclose pumps and piping used for waste management purposes. Each of these pits has a floor drain that opens into the tank dome and thus represents a leak path from the pit to the tank dome. The pits are covered from above by a concrete cover block or steel plate. Leak paths around the mating surfaces between cover and pit may allow air inleakage and outleakage that bypasses the filtered vent.

4.2.2 Cascade Inlet Lines

Tank C-103 is the third tank in a three-tank cascade. A sloped 76.2 mm (3-in.) pipe connects tank C-103 to tank C-102. A similar pipe connects tank C-102 to tank C-101. At present, waste levels in all of the three tanks are well below the cascade pipes, so no waste transfer by this route is possible. These pipes provide a connection between headspace gases in the three tanks.



H9312027.1

Figure 4-1. Schematic Cross-Sectional View of Tank C-103.

WHC-SD-WM-SARR-001 REV. 0

4.2.3 Ventilation System

Typical of most single-shell tanks, the headspace of the tank is passively vented to the atmosphere through a HEPA filter. Unlike other tanks, sorbent traps are also provided to trap noxious vapors that pass through the HEPA filter. An alternative venting arrangement, wherein the vent line valve on tank C-103 is closed, causes air flow through the cascade pipe (see Figure 4-1) into the headspace of tank C-102. Combined air flows from tanks C-103 and C-102 would vent to the atmosphere through the HEPA filter installed on the atmospheric vent from tank C-102. The presence of the cascade pipes that interconnect the three tanks (C-101, -102, and -103) allows for venting of one or all of the tanks through any one of the three filtered tank vents.

As depicted in Figure 4-1, an exhauster can be connected to the tank for purging the headspace with air. An exhauster has been used at various times at tank C-103. Recent uses of an exhauster and its impact on evaporation of water and organic liquid are discussed by Claybrook and Burke (1991). Currently, the tank is passively vented to the atmosphere through tank C-102. Potential flow paths include the cascade pipe, the filtered vent on tank C-102, and leak paths from the access pits to the atmosphere.

4.2.4 Thermocouple Tree

A single thermocouple tree was installed in riser R-1 located approximately 1.5 m (5 ft) from the wall of the tank in the southern quadrant. Temperatures in the tank are measurable from an aboveground junction box. Readings are taken manually on a weekly basis (Hanlon 1993). Thermocouples are located at 0.37 m (1.2 ft), 0.98 m (3.2 ft), 1.59 m (5.2 ft), and 4.88 m (6 ft) above the centerline bottom of the tank.

4.2.5 Waste Level Measurement

Waste level is measured automatically by a so-called FIC* gauge. This gauge detects the surface elevation by means of an electrical continuity measurement. The surface elevation is determined by the measured length of cable that supports the detector. Manual measurements also may be made with the FIC gauge system. For tank C-103, the FIC gauge readings are in inches, referenced to tank bottom at the sidewall. Waste depth referenced to the bottom center of the tank are 0.305 m (12 in.) greater than the FIC gauge reading. An air purge of 0.7 to 1.4 m³/h (25 to 50 ft³/h) is injected into the tank riser in which this instrument is installed to minimize the condensation of water vapor within the instrument. The instrument purge air flows into the tank headspace and is vented from the tank through the filtered vent system.

*Food Instrument Company.

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5.0 DESCRIPTION OF WASTE AND STORAGE CONDITIONS

The total volume of waste stored in tank C-103 is 739 m³ (195,000 gal) (Hanlon 1993). This volume is calculated from surface level measurements that are obtained from the FIC gauge installed in this tank (see Section 4.2.5 for gauge description). This total waste volume corresponds to a waste depth of 1.98 m (78.1 in.) referenced to the bottom center of the tank. Because the center of the tank floor is 1 ft (0.31 m) lower than the floor near the walls, total waste depth varies from 1.68 m (66.1 in.) to 1.98 m (78.1 in.) depending on radial distance from the center.

Sludge depth is between 0.76 m (30 in.) (Hanlon 1993) and 1.72 m (67.5 in.) referenced to tank centerline bottom. The smaller depth 0.76 m (30 in.) is a value reported by Hanlon (1993) and is based on readings obtained with a sludge level measurement device*. The highest depth 1.72 m (67.5 in.) is based on the height of solids collected in a core sample taken ~ 1.5 m (5 ft.) from the tank wall on the southern quadrant (see Appendix C for core sample details). A core sample taken from a location ~ 1.5 m (5 ft) from the tank wall on the northern quadrant indicated a sludge depth of 1.2 m (48.5 in.). These sludge level differences suggest that the sludge/supernatant interface is not level. Based on the difference between total waste depth and sludge depth, the depth of supernatant liquid is calculated to vary from approximately 0.28 m to 1.23 m (10.9 in. to 48.4 in.).

5.1 ORGANIC LIQUID

Samples of the organic liquid taken in December 1993 have been analyzed by several procedures to evaluate flammability and exothermic reaction hazard potential.

5.1.1 Depth of Organic Liquid Layer

Visual observations and physical measurements performed during the December 1993 sample retrieval exercise provide evidence that the organic liquid thickness is between 3.8 cm and 5.1 cm (1.5 in. and 2.0 in.) (Huckaby 1994b). The organic-aqueous interface level, measured from a riser flange, was detected by means of a conductivity probe. This interface was measured to be 33 ft 0.125 in. (10.06 m) below the riser flange. Visual observations of sample bottle filling (air bubbles escaping during liquid filling), along with measurements of bottle position relative to the riser flange, yielded an air-organic liquid interface position of

*A sludge level measurement device is a weighted plummet, suspended by a measuring tape, that is manually lowered onto the sludge through a tank riser. The operator reports the sludge level as the depth where the sludge weight is supported by the solids (i.e., the measuring tape develops slack).

32 ft 10.5 in. (10.02 m) below the riser flange. Given the uncertainties of these measurements, Huckaby (1994b) provides an estimate for organic liquid depth of 1.5 to 2.0 in. (3.8 to 5.1 cm).

This estimate of organic liquid depth is significantly smaller than the depth, 10 in. to 13 in. (25 cm to 33 cm), estimated on the basis of volumes of organic liquid thought to have been transferred from tanks C-102 and C-104 (Hopkins 1992, Agnew 1993). The diminished volume of liquid, and the apparent depletion of more volatile components (see Section 5.1.3) are consistent with the evaporation of organics during periods of forced ventilation of headspace air in tank C-103.

5.1.2 Flashpoint

The flashpoint of the organic liquid was measured directly in a flashpoint apparatus and has been computed from two sets of composition data. The three independent data sets yield similar flashpoints.

Four samples of the organic liquid were pretreated by contacting with granular anhydrous calcium sulfate to remove water, and then subjected to flashpoint determination (Pool and Bean 1994). The instrument used was Grabner Instruments* CGA-FLP Miniflash Flash Point Tester (WD 16835), distributed by PETROLAB Corporation. The procedure followed ASTM Setaflash Closed Cup Methodology (ASTM D 3278-90) by measuring the flashpoint on samples that were temperature equilibrated before introduction of an electric spark. The flashpoint is defined as the temperature where a deflagration produces a pressure pulse of 4 kPa or more.

This test unit was selected for the present purpose because it uses a small volume (2 ml) of the organic liquid. The use of small liquid volumes was desirable because of the need to minimize the required volume of sample and to minimize radiation exposure to operating personnel.

As noted above, the organic liquid was contacted with anhydrous calcium sulfate to remove dissolved water. Calculation indicated that water volatilized from the liquid could have inerted the vapor phase of the test unit (vapor volume equal to liquid volume), but was insufficient to inert the headspace air in tank C-103 (vapor volume large compared to liquid volume). The flashpoint of anhydrous liquid is expected to be equal to or lower than for untreated liquid which contains a measured 1.3 wt% water (Pool and Bean 1994), and therefore is conservative from a safety standpoint.

Results of the flashpoint determinations are summarized as follows.

*Grabner Instruments, Latham, New York.

Table 5-1. Measured Flashpoint of C-103 Organic Liquid (Pool and Bean 1994).

Sample No.	Temperature, °F or °C		
	No Flash, °F(°C)	Observed Flash, °F(°C)	Flashpoint, °F (°C)
1	240 (116)	245 (118)	243 (117)
2	245 (118)	248 (120)	247 (119)
3	245 (118)	247 (119)	246 (119)
4	245 (118)	250 (121)	247 (119)
Average			246 (118)

The "No Flash" temperature is the highest equilibrated sample temperature where a flashpoint was not detected. The "Observed Flash" temperature is the lowest sample equilibrated temperature where a flash was detected. "Flashpoint" is the average of "No Flash" and "Observed Flash" temperatures. The instrument, as operated for this application, yielded a flashpoint for a certified n-dodecane standard of 185 °F which is within the ASTM acceptance window of 184 ± 4 °F for this standard substance (Pool and Bean 1994).

The measured flashpoint may be compared to values calculated from two data sets as described in Appendix A. First, the flashpoints predicted from the measured organic liquid component concentrations fall between 105 °C and 114 °C depending on assumptions made. Second, the lowest flashpoint calculated from measured vapor concentrations is 96 °C. All of the flashpoints, measured and calculated are higher than higher than 93.3 °C (200 °F), and according to Table 3-1, the liquid fits the lowest NFPA classification, IIIB.

5.1.3 Liquid Composition Measured by GCMS

Analysis of the liquid by Gas Chromatographic/Mass Spectrometry (GCMS) yielded the following composition (Pool and Bean 1994).

Table 5-2. Composition of Organic Liquid Sample Taken From Tank C-103 (Pool and Bean 1994).

Analyte	Measured weight percent
Dodecane	2.8
Alkane-1*	0.2
Alkane-2	1.1
Tridecane	11.4
Alkane-3	0.5
Alkane-4	1.0
Tetradecane	6.0
Alkane-5	0.7
Pentadecane	0.9
Dibutyl butyl phosphonate	1.9
Tributyl phosphate	47.2
Total recovery	73.7

*Branched chain alkanes having volatilities intermediate between the listed normal alkanes.

Based on the above analysis, the mass ratio of NPH to TBP is 33:67 (all alkanes included in NPH and DBBP included with TBP). This ratio shows that TBP accounts for more of the liquid mass than does NPH. For the original mix (~70% NPH on a volume basis), the mass ratio of NPH to TBP is calculated to be 65:35. The enrichment of the mix in TBP is consistent with the stripping of the more volatile alkane components during periods of forced ventilation of the headspace of tank C-103. The measured ratio of NPH:TBP calculated from the data of Table 5-2 (33:67) is close to a value (27:73) calculated from data reported by Prentice (1991). Prentice (1991) analyzed a sample of the organic liquid taken in 1991.

Based on the analytical recovery of 73.7%, some 26.3 wt% of the organic liquid was not detected in the GC/MS. While the chemical structure of this undetected material is unknown, the other test results (Sections 5.1.4, 5.1.5, and 5.6) provide evidence that the unknown material does not represent a safety hazard with respect to uncontrolled exothermic chemical reactions.

5.1.4 Vapor Composition in Equilibrium with Liquid

A sample of the organic liquid was heated in a closed vial to temperatures of 40 °C, 70 °C, and 100 °C (Pool and Bean 1994). A vapor space above the liquid was allowed to

equilibrate with the liquid, and was then sampled. The vapor space sample was analyzed by a GC/MS instrument, with results reported as mass concentrations in the vapor space. Results for NPH-TBP components are as follows.

Table 5-3. Vapor Concentration of NPH-TBP Components in Equilibrium with Liquid at Three Temperatures (Pool and Bean 1994).

Component	Mass concentration (mg/L)		
	40 °C	70 °C	100 °C
Undecane	0.06	0.22	1.46
Dodecane	0.32	2.4	13.8
Alkane-1*	0.05	0.32	2.2
Alkane-2	0.08	0.62	3.6
Tridecane	0.46	4.2	18.2
Alkane-3	0.07	0.36	0.64
Tetradecane	0.22	1.2	6.4
Alkane	0.03	0.11	0.68
Pentadecane	0.02	0.12	0.70
DBBP	0.01	0.04	0.58
TBP	0.14	0.78	8.4
Total	1.46	10.37	56.66

*Branched chain alkanes having volatilities intermediate between the listed normal alkanes

The vapor phase concentrations listed in Table 5-3 are consistent with concentrations based on independent measurements and calculations:

1. The Table 5-3 concentration of NPH components at 40 °C sum to 1.31 mg/l. This value agrees well with the NPH concentration (1.2 ± 0.25 mg/L) determined from samples withdrawn from headspace air in tank C-103 (Goheen 1994) during December 1993, when headspace air temperature was measured to be 40 °C. Headspace air sampling data are presented in Section 5.6.
2. The measured concentrations agree reasonably with values computed from the liquid composition (Table 5-2 values) using Raoult's Law. Comparisons of measured and predicted vapor concentrations are provided in Appendix A.

The agreement of vapor concentrations determined by independent means supports the validity of the measurements, and provides confidence that NPH-TBP concentrations in headspace air can be predicted as a function of temperature. As described in Section 6, the variation in combustible vapor concentration with temperature is important in assessing the flammability hazard posed by the organic liquid.

5.1.5 Adiabatic Calorimetry Tests

These tests were carried out to quantify the energy that could be liberated by organic-nitrate/nitrite reactions in the organic liquid. The hazard posed by organic-nitrate/nitrite reactions, as described in Section 3.4.3, is significant only if exothermic reactions release enough energy to cause the overpressurization of headspace air.

Three tests, each using approximately 10 g of organic liquid from tank C-103, were carried out in an adiabatic calorimeter under a nitrogen overpressure of 2.76 MPa (400 lb/in² gauge). The relatively high gas overpressure was used to increase the boiling point of the organic liquid to above the onset temperatures of organic-nitrate/nitrite reactions. While the use of the nitrogen overpressure is not realistic of tank pressure (1 atm), the overpressure would prevent the boil-off of volatile nitrated organic compounds at low temperatures. If nitrated organic compounds were present and boiled off at temperatures below their reaction onset temperature, no exothermic reactions would be observed in the calorimeter. The relatively high liquid temperatures achieved in these tests (300 to 400 °C) are well beyond the reaction onset temperatures for organic-nitrate reactions that could pose a hazard in tank C-103.

Results of the three adiabatic calorimetry tests performed on organic liquid samples retrieved from tank C-103 are described in detail in Appendix B. The key result of the tests is that exothermic reactions caused only minor degrees of self-heating (<40 °C) and generated negligible quantities of noncondensable gases. These results provide evidence that organic-nitrate/nitrite reactions do not pose a safety hazard for the organic liquid currently in tank C-103.

The absence of significant exothermic reactions in the organic liquid, as indicated by adiabatic calorimetry tests, is consistent with the analyzed nitroalkane concentration. Pool and Bean (1994) analyzed the C-103 organic liquid for primary and secondary nitroalkanes by means of Fourier Transform Infrared (FTIR) spectroscopy and reported concentrations to be below the detection limit of 0.01 wt% as NO₂.

5.2 AQUEOUS SUPERNATANT LIQUID

Duplicate samples of the aqueous supernatant liquid in tank C-103 were analyzed for major components (Edrington 1991). Results are shown in Tables C-1 and C-2 in Appendix C.

An independent set of analytical results, determined on samples taken in December, 1993 (Pool and Bean 1994) corroborate the compositional data of Edrington (1991).

Solutes are mainly sodium nitrite and sodium sulfate at a pH of 9.5. The concentrations of nitrite and sulfate, expressed in moles per liter amount to approximately 0.7M and 0.3M, respectively. Organic carbon concentration is approximately 7.5 g/L. As compared to many Hanford Site wastes, this solution is quite dilute, and is relatively high in sulfate.

5.3 SLUDGE

The sludge in tank C-103 has been characterized by analyses of two push-mode core samples taken in 1986. Information from the analytical report (Weiss and Schull 1988) is presented in Appendix C. Key results from the analysis of the two cores include the following.

- The dominate heat-producing nuclide is ⁹⁰Sr. This analytical finding is in agreement with tank contents based on waste transfer records (Agnew 1993).
- Total waste depth (sludge and supernatant liquid) estimated from the two core samples (2.0 m or 6.6 ft) agrees well with the value based on interface level measurements (2 m or 6.5 ft) reported by Hanlon (1993).
- Total organic-carbon concentrations were measured to be 3.9 and 2.61 g/kg for the two core samples. As shown in Section 6.3, these concentrations are below a level where organic-nitrate reactions become a hazard.

5.4 TEMPERATURE

Temperatures in tank C-103 are measured weekly by manual read-out of thermocouples located along a vertical line at one location as described in Section 4.2.4, and as shown schematically in Figure 4-1. Based on a comparison of thermocouple positions (Section 4.2.4) and waste depths (Sections 5.1, 5.2, and 5.3), the thermocouples appear to be located in the waste as follows:

- No. 1 is low in the sludge
- No. 2 is in the upper portion of the sludge
- No. 3 is in the higher portion of the aqueous supernatant liquid, and
- No. 4 is in headspace air, approximately midway between the waste surface and the tank dome.

Recorded temperatures for the past three years are exhibited in Figure 5-1.

As illustrated by the data trends of Figure 5-1, temperatures rise and fall as a result of the annual changes in aboveground temperatures. The highest temperatures are in the sludge, thermocouples 1 and 2. Decay heat is dissipated by conduction in the sludge and by a combination of conduction, convection, and radiation in the liquid and air spaces of the tank. Temperatures decrease in the upward vertical direction as heat flows down the temperature gradient into the environs.

Several spurious data points, taken early in 1991, are included on Figure 5-1 to illustrate errors in recorded data. The spike shown for April 20, 1991 (thermocouple 1 goes from 124 °F to 133 °F and then back to 123 °F) is clearly an artifact. The data sheet for the day indicated the use of "wrong instrument." The thermal inertia of the sludge is too large for it to undergo spike-like changes in temperature. When apparently incorrect data are eliminated, the waste temperatures respond as expected to the annual temperature cycle.

Transient conduction of heat through soil overburden results in a phase shift of tank temperatures as compared to atmospheric temperatures. Average temperatures (mean between seasonal peaks and valleys) occur in mid-January and June each year. The highest tank headspace temperature occurs on approximately October 15 and the lowest temperature on approximately April 15. These phase shifts are potentially important in causing fog droplets to form in headspace air during a part of the temperature cycle.

5.5 SURFACE LEVEL

Surface level readings for a 6-year period for tank C-103 are presented in Figure 5-2. Comments that help identify the significance of the surface level measurements are as follows.

- The level has declined slowly, approximately 0.9 in. over the last 6 years. This decline is consistent with the loss rate expected for evaporation (Claybrook and Burke 1991).
- The absence of periodic increases and decreases in level is evidence that tank C-103 does not experience episodic gas releases similar to those experienced in tanks on the Flammable Gas Watch List.
- Purging of the headspace with atmospheric air leads to a discernable lowering of waste level by evaporation. This is evidenced by the observable drop in level in the fourth quarter of 1989, a period when a portable exhauster was used to ventilate the headspace of tank C-103.

Figure 5-1. Waste Temperatures in Tank C-103.

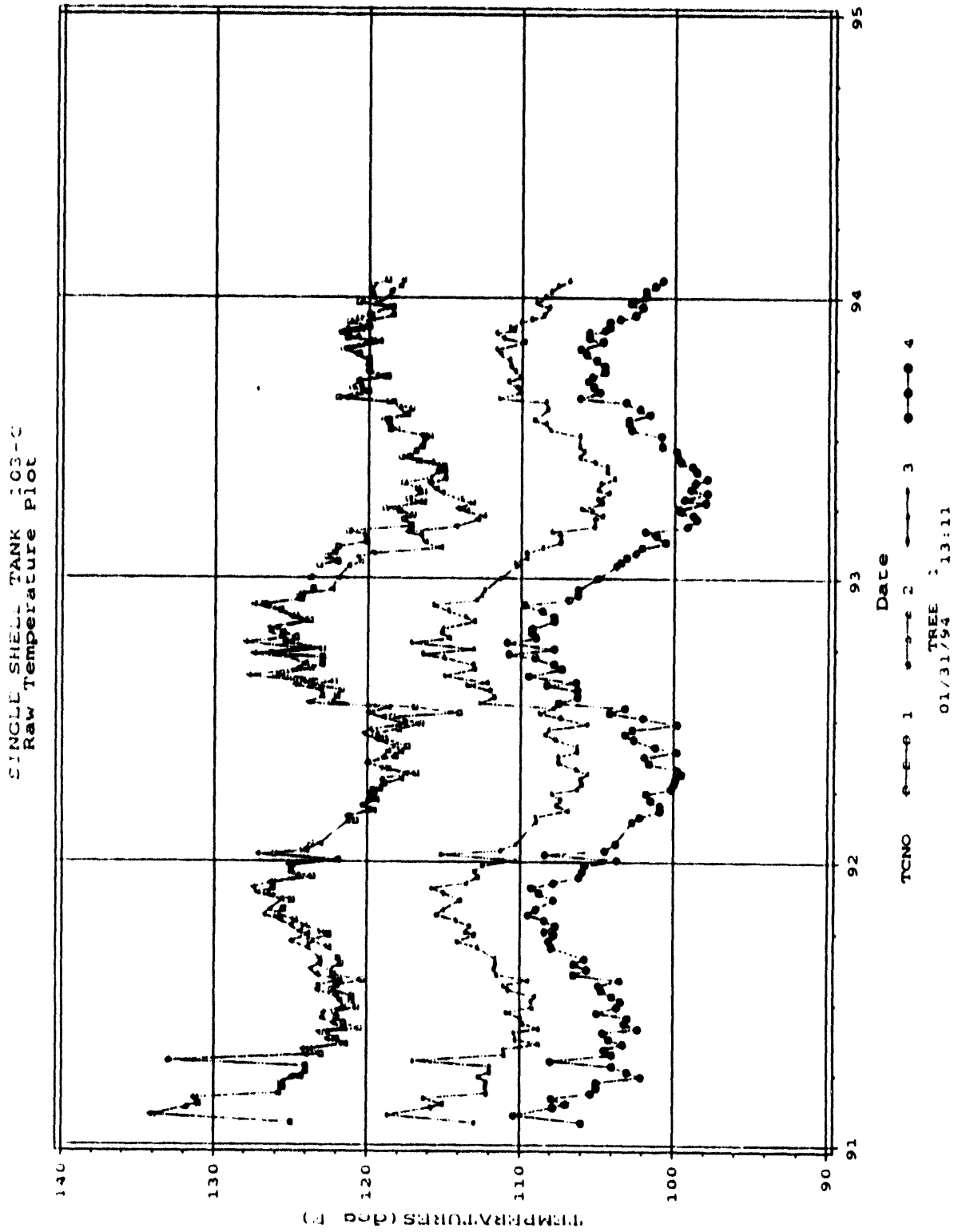
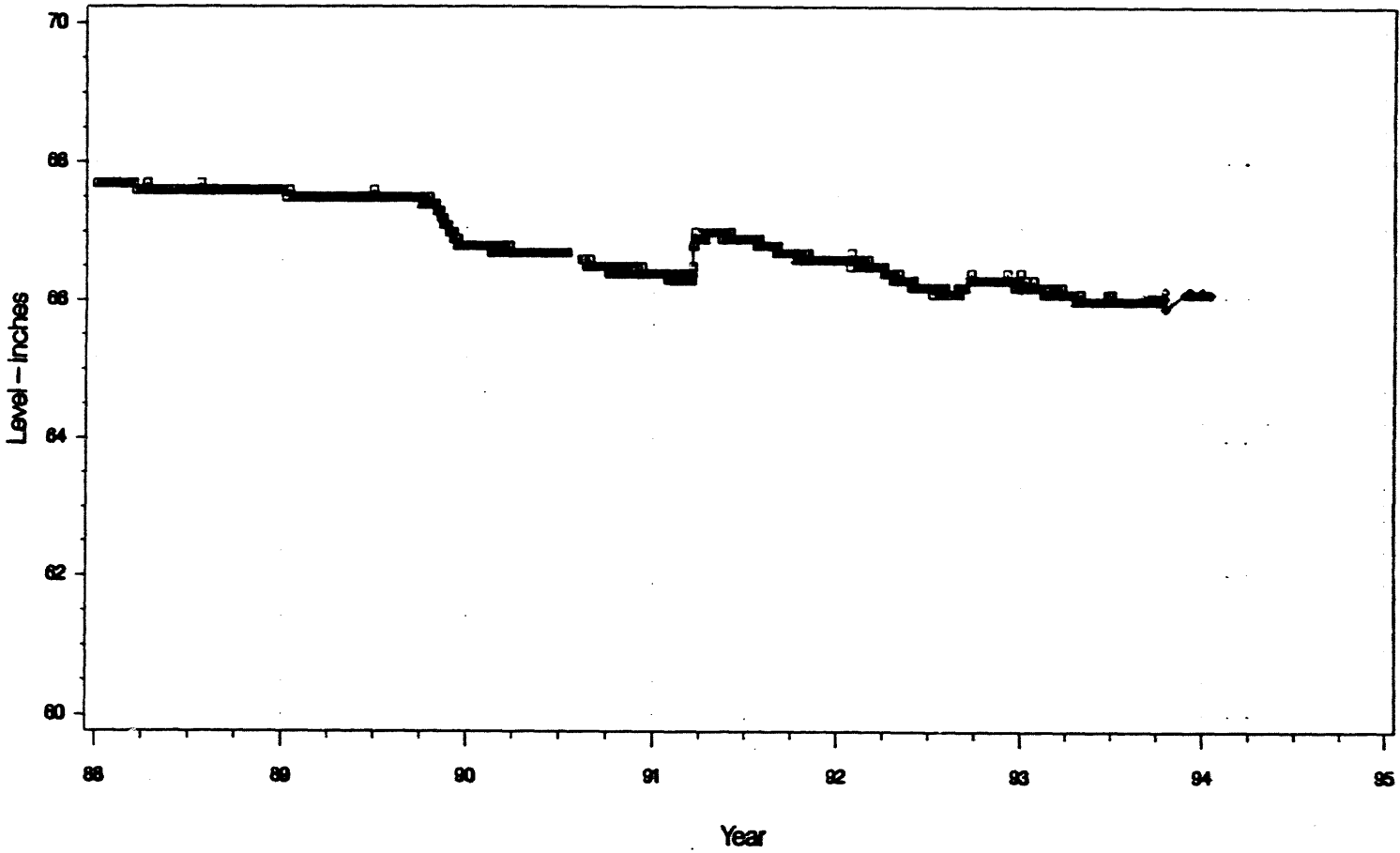


Figure 5-2. Tank C-103 Surface Level Readings.



Data From Surveillance Analysis Computer System
Prepared By Surveillance & Data Acquisition
Only 'Good' Data Displayed

Square - Automatic FIC Diamond - Manual FIC

000001 0.00

- The indicated increase in level in the first quarter of 1991 reflects the addition of approximately 4.1 m³ (1080 gal) of water to the tank. The water was used to pressure test waste transfer pipes connected to tank C-103.
- The level has remained essentially constant during the latter part of calendar year 1993. The reduced evaporation rate is attributable to the sealing of pit cover leak paths on April 11, 1993.

5.6 COMBUSTIBLE SPECIES IN HEADSPACE AIR

Combustible species in headspace air in tank C-103 could be produced by three mechanisms:

1. Radiolytic and chemical degradation of hydrocarbons and water
2. Formation of aerosols of organic materials
3. Evaporation of organic liquid.

Each of these mechanisms is expected to result in an equilibrium concentration in headspace air that would change only slowly with time. This relative constancy with time is in contrast with tanks on the Flammable Gas Watch List of the Hanford Site (Hanlon 1993) in which episodic releases of trapped gas may occur. The absence of significant episodic gas releases is evidenced by the following empirical observations.

- The waste surface level does not undergo periodic slow increases followed by rapid decreases that characterize tanks that undergo episodic gas releases (see Figure 5-2).
- There is no evidence that periodic temperature inversions in the waste take place (see Figure 5-1). Temperature inversions are associated with waste "roll-over" in tank 101-SY, which is known for its episodic gas releases (Leach and Stahl 1993b).

Based on these observations, it is concluded that headspace flammability can be evaluated from representative samples taken under quasi-equilibrium conditions, and that episodic gas releases are unimportant for this tank.

5.6.1 Combustible Gases

Combustible gas concentrations have been measured in headspace air by several sampling and analytical procedures (Huckaby 1994a, 1994c, Goheen 1994).

COMBUSTIBLE GAS METER

A combustible gas meter (CGM),* calibrated with pentane before and after use, yielded readings of 4% to 7% of the LFL when an inlet tube drew air from the upper part of the tank headspace (Huckaby 1994a). A major part of this reading may be attributed to hydrogen. Based on a hydrogen concentration of 2% of the LFL (from measurements described later in this section) and a meter response factor of 2 for hydrogen (response factors provided by the manufacturer of the CGM), a CGM reading of 4% LFL is attributable to hydrogen. The additional 3% LFL (7% - 4%) may be attributed to the other combustible gases present in sampled air.

NORMAL PARAFFIN HYDROCARBONS AND TRIBUTYL PHOSPHATE

The concentration of NPH and TBP in headspace air was determined from samples taken within the headspace, approximately 0.92 m (3 ft) above the waste surface (Huckaby 1994a, Goheen 1994). Both vapor and aerosol (if any) were collected on a filtered adsorber bed sampler, called Occupational Safety and Health Administration (OSHA) versatile sampler (OVS for short). The organic material collected on the OVS was desorbed using carbon disulfide, and quantitatively analyzed using a gas chromatographic/mass spectrometer (GCMS) device. The validity of this sampling and analytical method is supported in a laboratory study at PNL (Ligotke 1993).

Mass concentrations of normal alkanes determined by the above described for samples taken in December 1993 are summarized in Table 5-4.

Table 5-4. NPH Concentrations Measured in OVS traps from Tank 241-C-103 (From Huckaby 1994a).

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	0.047	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	0.578	0.578	0.140	<0.003	1.067

*Model TMX-410, Industrial Scientific Co., Oakdale, PA, 15071.

Based on a study of uncertainties, Goheen (1994) recommends that OVS samples 8, 9, and 10 be used to quantify NPH concentrations. Total NPH concentrations and other particulars are presented in Table 5-5.

Table 5-5. Total NPH Mass Concentration in OVS Samples From C-103 (Goheen 1994).

Sample	Actual sample volume (L)	Total NPH mass (mg)	NPH concentration (mg/L)	Uncertainty (mg/L)
OVS 8	4.40	4.69	1.07	0.22
OVS 9	4.41	4.91	1.11	0.23
OVS 10	4.41	4.71	1.07	0.22

Based on the three samples described in Table 5-5, the NPH concentration in the vapor space of C-103 is 1.08 ± 0.23 mg/L.

Compounds other than NPH analytes were indicated in the OVS sample GC/MS chromatograms. Except for TBP, these compounds were not quantified. An initial screening of the spectra indicated that the compounds were branched alkanes (Goheen 1994). The NPH compounds listed in Table 5-4 constituted about 90% of the portion of the material present on the OVS that can be detected by GC/MS (Goheen 1994). An estimate of total alkanes can be obtained by multiplying the concentrations in Table 5-5 by a factor of 1.1.

TBP was detected in low concentrations. Its concentrations were estimated by Goheen (1994) to be approximately 45 mg/m³ or 4.3 ppm by volume.

The estimated total concentration of NPH of $1.2 \text{ mg/L} \pm 0.25 \text{ mg/L}$ (Table 5-5 values increased by 10%) amounts to $2.6\% \pm 0.5\%$ of the LFL of 47 mg/L (Huckaby and Estey 1992). This concentration represents vapors and aerosol particles in total. It is evident from these results that the constituents of NPH have too low a vapor pressure to constitute a flammability hazard in tank C-103 under current conditions. This finding supports a conclusion in an earlier study of C-103 safety (Borsheim and Kirch 1991).

HYDROGEN, CARBON MONOXIDE, AND METHANE

The concentrations of H₂, CO, and CH₄ in headspace air in tank C-103 have been determined from samples taken in January 1994 (Huckaby 1994c). A heated sampling probe was used to withdraw headspace air into evacuated stainless steel containers. The canisters were shipped to several independent laboratories where the gas samples were analyzed for combustible constituents. Key results, for H₂, CO, and CH₄ are listed in Table 5-6.

Table 5-6. Concentrations of H₂, CO, and CH₄ Measured in Headspace Air in January 1994 (Huckaby 1994c).

Component	Concentration, PPMV	Std. deviation
H ₂	805	18
CO	23.9	0.9
CH ₄	15.9	0.5

The data of Table 5-6 indicate that hydrogen is the dominant specie, amounting to 0.08% on a volumetric basis. This hydrogen concentration represents $(0.08/4) \times 100$ or 2% of the LFL for hydrogen. CO and CH₄ concentrations, expressed as percent of LFL, amount to 0.02% and 0.03% respectively.

AMMONIA

The concentration of ammonia (NH₃) in headspace air in tank C-103 was determined from samples taken in January 1994 (Huckaby 1994a). Ammonia was collected on sorbent tubes and analyzed using an ion selective electrode. Three liters of air, withdrawn through a heated sampling probe, was passed through each ammonia sorbent tube.

Results for samples collected on three days in January 1994 are listed in Table 5-7.

Table 5-7. Ammonia in Tank C-103 Headspace air in January 1994 (Huckaby 1994c).

Day	NH ₃ collected, micro moles	Concentration, ppmv
1	34	291
2	55	471
3	40	342
Average		368

The average of the three measurements, 368 ppmv, is 46% of the average hydrogen concentration (see Table 5-6). Since the LFL of ammonia is 15% by volume (Lewis and Von Elbe 1987) the highest measured concentration, 471 ppmv, represents only $(0.0471/15) \times 100 = 0.3\%$ of the LFL. This is small compared to the 2% of LFL represented by the average hydrogen concentration.

TOTAL NON-METHANE HYDROCARBONS

The contents of the stainless steel canisters referred to earlier were analyzed for total non-methane hydrocarbons (Huckaby 1994c). Results of analysis of 18 samples, yielded the following result:

$$\text{Average} = 2.3 \text{ g/m}^3$$

$$\text{Std. deviation} = 0.40 \text{ g/m}^3.$$

This value, 2.3 g/m^3 , may be compared to measured concentrations of organic vapors in equilibrium with the liquid, 1.46 g/m^3 (Table 5-3), and measured NPH concentrations in tank headspace air, 1.2 g/m^3 (Table 5-5 values increased by 10%). It is apparent from this comparison that NPH/TBP vapors make up a major fraction of total organic vapors.

Because many hydrocarbons have similar LFL values when expressed in terms of mass concentration (Zabetakis 1965), the contribution of organic gases to LFL may be estimated on the basis of an LFL of 47 g/m^3 , an average value for NPH constituents (Huckaby and Estey 1992). The contribution of organics to the LFL is estimated to be:

$$(2.3/47) \times 100 = 4.9\% \text{ LFL}$$

ORGANIC AEROSOLS

Visual observation made during a December 1993 sampling showed that no visible aerosol was present in the bulk of headspace air (Huckaby 1994). Based on a correlation of visual range vs aerosol concentration (Hilliard et al. 1979) and the observation that visual range was much greater than 10.1 m (33 ft) an aerosol concentration of much less than 0.3 mg/L is indicated.

The concentrations of NPH exhibited in Table 5-5 is the sum aerosol and vapor mass. A major fraction of measured concentration, approximately 1.2 mg/L , is attributable to vapor, with little, if any, contribution from aerosols.

As discussed in Section 6.0 of this report, an aerosol has been observed in tank C-103 in the past. Because temperatures in the tank undergo seasonal cycles, it is possible that aerosols could form in the future. The maximum concentration, predicted on the basis of a technical analysis (Section 6.0), is small (less than 1%) compared to the LFL of 47 mg/L .

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6.0 PHENOMENOLOGY OF IDENTIFIED HAZARDS

The technical discussions described in this section were formulated to help answer the following questions.

1. What consequences could result from the hazard?
2. What conditions and parameters govern postulated accident behavior?
3. Under what conditions could a risk-significant accident actually occur?
4. What information is needed to quantitatively assess the identified hazard?

6.1 DEFLAGRATION IN HEADSPACE AIR

The accident scenario for this hazard involves the formation of a flammable mixture in headspace air with assumed subsequent ignition. A combustion wave is then assumed to propagate at subsonic velocities through the air-fuel mixture, raising its temperature and pressure. The increased pressure represents a threat to tank structural integrity and could cause uncontrolled venting of headspace gases to the atmosphere.

6.1.1 Internal Pressures Generated by a Postulated Hypothetical Headspace Deflagration

To put this hazard into perspective, a hypothetical deflagration in headspace air was analyzed. The fuel loading was parametrically varied from the LFL to the stoichiometric concentration (where all oxygen is consumed). For simplicity, the fuel was assumed to be n-dodecane ($C_{12}H_{26}$). This hydrocarbon species is a major component of fresh NPH (Beary 1970). Because the specific enthalpy of reaction is similar for all of the normal alkanes in NPH, results of the deflagration pressure calculations are insensitive to assumed composition.

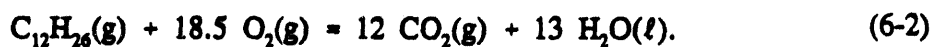
For an adiabatic constant volume combustion process, no work is done so the change in internal energy of combusted gases is equal to the heat of combustion. Equating the changes in internal energy (Hougen et al. 1954):

$$\Delta E_c = - \int_{T_1}^{T_2} n_i C_{v_i} dT \quad (6-1)$$

where:

- ΔE_c = Combustion energy, J/mole
- n_i = Number of moles of product specie i
- $C_{v,i}$ = Heat capacity at constant volume of specie i, J/mole °K
- T_1 = Initial temperature, °K
- T_2 = Final temperature, °K
- T = Temperature of burned gas, °K.

The stoichiometry of the combustion process was based on reactions to form water and carbon dioxide:



The change in enthalpy for this reaction is given by Lewis and Von Elbe (1987) as

$$\Delta H_{298}^{\circ} = -1944.4 \text{ Kcal/g-mole } C_{12}H_{26}$$

for liquid water as a product. For our case, water will be a gas, so the enthalpy of vaporization must be added. The change in enthalpy for water evaporation is given by Lewis and Von Elbe (1987) as:

$$\Delta H_{298}^{\circ} = 10.503 \text{ Kcal/g-mole } H_2O.$$

The change in enthalpy for reaction (6-2) is thus:

$$\Delta H_{298}^{\circ} = -1944.4 + (13)(10.503) = -1807.9 \text{ Kcal/mole.}$$

Finally, ΔE_i can be calculated from the relationship between enthalpy and internal energy for an ideal gas (Daniels and Alberty 1955):

$$\Delta E = \Delta H - \Delta nRT \quad (6-3)$$

where:

- ΔE = Change in internal energy
- ΔH = Change in enthalpy
- Δn = Change in gas moles
- R = Gas constant
- T = Absolute temperature.

Substituting numerical values in Equation (6-3)

$$\Delta E_i = -1,807,900 - (5.5)(1.987)(298)$$

$$\Delta E_i = -1,811,156 \text{ cal/g mole } C_{12}H_{26}.$$

This energy of combustion amounts to $3.26 \text{ E}+06 \text{ Btu/lb mole}$.

The LFL for n-dodecane is given by Zabetakis (1965) as 0.60% by volume. Stoichiometry calculations based on Equation (6-2) indicate that a reaction at the LFL would consume 58% of initial oxygen present. An initial fuel loading of 1.034% by volume would react with 100% of oxygen present and thus represents the most energetic reaction possible. The quantities of dodecane required for the LFL and stoichiometric burn in C-103 are calculated to be 100 kg (220 lb) and 190 kg (415 lb), respectively. Translated to thickness of liquid in the floating layer, these quantities correspond to depths of 0.3 mm (0.012 in.) and 0.6 mm (0.022 in.), respectively. Only a small part of the organic inventory could be combusted by oxygen available in headspace air.

Results of calculations based on Equations (6-1), (6-2), and (6-3) are portrayed in Figure 6-1 where internal gas pressure is plotted as a function of initial fuel loading. The data of Figure 6-1 shows the calculated pressures vary from 530 kPa gauge (77 lb/in²) at the LFL to 820 KPa gauge (119 lb/in²) at the stoichiometric limit. All calculated pressures from combusting burnable mixtures exceed tank structural capabilities.

Three factors prevent ideal pressures from actually being achieved:

1. Incomplete combustion
2. Heat transfer from the gas to surfaces
3. Gas leakage.

The importance of these three factors was explored by developing simple mathematical models which could be used to estimate the reduction in peak pressure due to each of them. In all cases analyzed, it was assumed that fuel (dodecane) was mixed uniformly in the entire headspace air volume. Conclusions reached from the simple analysis performed are as follows.

1. Peak burn pressures calculated when the mitigating factors were accounted for were significantly less than ideal for cases where the fuel concentration was close to the LFL.
2. The combined effect of the three mitigating factors is too small to provide assurance that any global burn, for fuel concentrations higher than the LFL, would not result in pressures higher than the tank could safely withstand.
3. The deflagration hazard, if ignition is assumed, can be avoided only by ensuring that fuel concentrations in headspace air remain below the LFL.

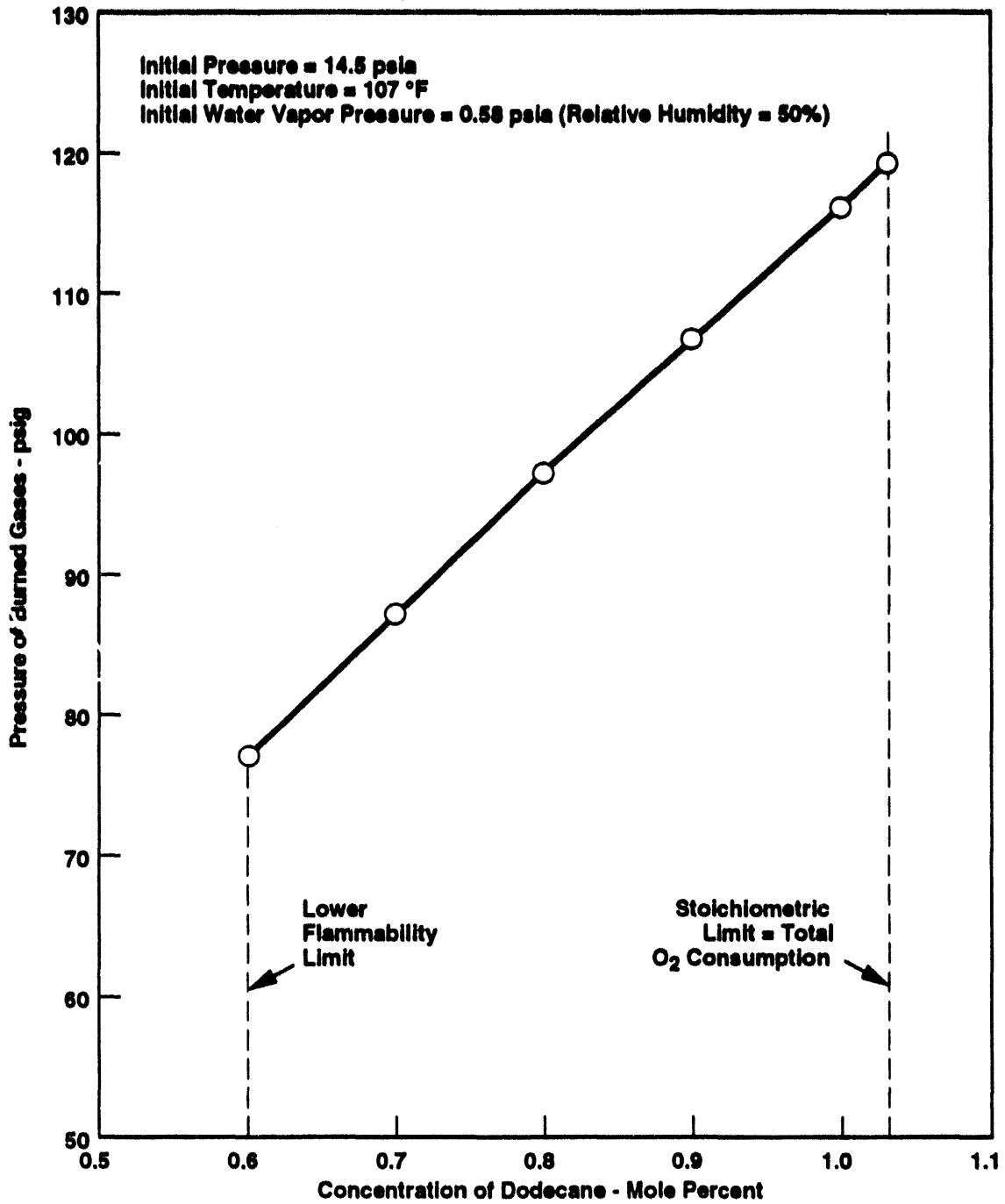
6.1.2 Generation and Buildup of Combustible Species in Headspace Air

The concentration of combustible species in headspace air can vary with time. At any point in time the concentration of combustible species is determined by a combination of the following waste properties and tank operating parameters:

- Headspace ventilation rate
- Venting pathway (directly to atmosphere versus venting through other tanks)
- Rate of generation of radiolytic gases (mainly H₂)
- Temperature of organic liquid
- Composition of organic liquid
- Time measured from last change in vent rate or flow path.

In this section the temporal variation in combustible species, in response to possible changes in ventilation flow rates, pathway configurations, and temperature, are analyzed. The objective is to provide a technical basis for operational controls that are necessary to prevent combustible gases from exceeding 25% of the LFL.

Figure 6-1. Calculated Pressure for an Adiabatic Constant Volume Burn of Dodecane in Air.



6.1.2.1 Radiolytic Species. Radiolysis can be expected to cause both polymerization of hydrocarbons and fragmentation with the loss of light molecules to the gas phase (Gerber et al. 1992). Radiolysis also generates hydrogen by decomposing water. While studies of radiolytic hydrogen generation in waste tanks have indicated that passive ventilation is sufficient to maintain the hydrogen concentration well below the flammable limit (Borsheim and Kirch 1991), no equivalent study has been made for light organic molecules. Given the complexity of radiolysis (Gerber et al. 1992), it appears that a realistic hazards analyses will have to be based on empirical measurements of flammable gas constituents in tank C-103.

A one-time measurement of gas phase concentrations must be interpreted in a way that accounts for the ventilation flow rate history, as discussed below.

The headspaces of tanks C-101, C-102, and C-103 are presently (March 1994) connected together as shown schematically in Figure 6-2. Several hypothetical cases will be analyzed to illustrate how the concentration of species produced by first order reaction kinetics would be expected to vary with time.

First consider the case of tank C-103 isolated from other tanks, and with headspace purging limited to passive breathing through the filter/trapping system. A source term, S_3 , measured in moles/day, is assumed to produce flammable species at a constant rate. A liquid layer is assumed to be present and in equilibrium with the gas phase. A differential equation may be written by means of a material balance on the gas phase.

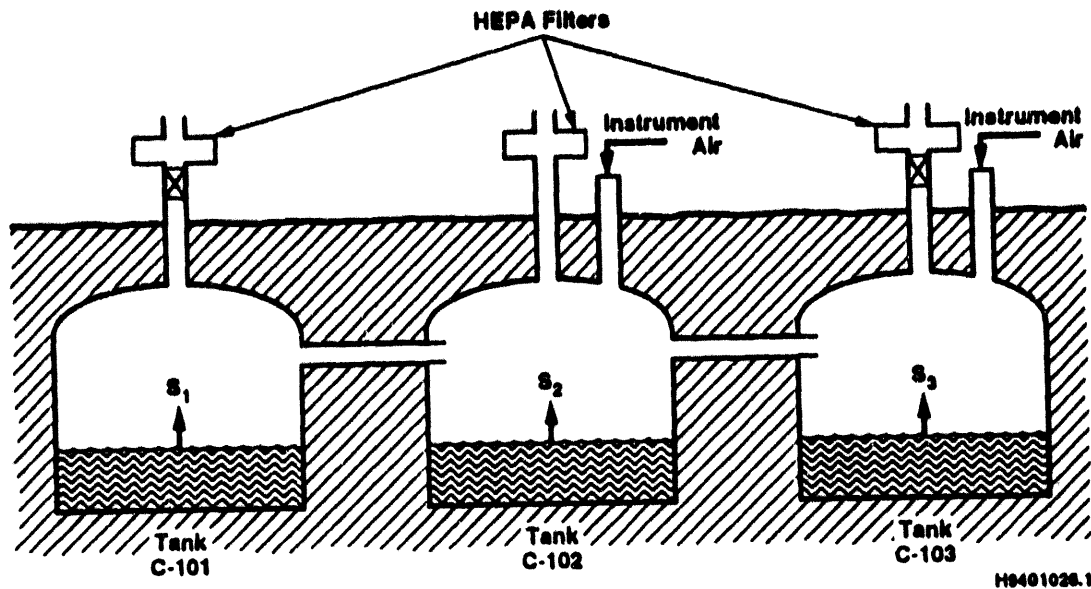
$$\text{Input Rate} = \text{Output Rate} + \text{Accumulation Rate}$$

$$S_3 = Q_3 C_3 + \frac{d}{dt}(C_3(V_g + HV_l)) \quad (6-4)$$

where:

- S_3 = Radiolytic production rate, moles/day
- Q_3 = Ventilation rate, m³/day
- C_3 = Concentration of flammable species, moles/m³
- t = Time, days
- V_g = Volume of gas space, m³
- H = Henry's law coefficient, dimensionless
- V_l = Volume of liquid, m³.

Figure 6-2. Schematic Diagram of Headspace Ventilation for Tanks C-101, C-102, and C-103.



Equation (6-4) can be solved easily in closed form if the source rate S_3 , the volumes V_g and V_t , ventilation rate Q_3 , and Henry's law coefficient are taken as constants. The result, for an initial concentration of zero, is

$$C_3 = \frac{S_3}{Q_3} (1 - \exp - \frac{Q_3 t}{V}) \quad (6-5)$$

where:

$$V = V_g + HV_t = \text{effective volume of gas.}$$

For long times, C_3 asymptotically approaches the value S_3/Q_3 , which is the source rate divided by the ventilation rate. This inverse dependency on ventilation rate is important in interpreting concentrations measured at one point in time. A change in ventilation rate by a factor of 10 would change the asymptotic concentration also by a factor of 10.

The time required to achieve 90% of the maximum concentration change may be derived from Equation (6-5) by solving for time when $C_3 = 0.9 S_3/Q_3$. The result is

$$t_{90} = 2.3 \frac{(V_g + HV_l)}{Q_3} \quad (6-6)$$

Note that t_{90} would be approximately the same for all species where H was smaller than approximately 10. For larger values of H (highly soluble species) buildup of solute in the liquid phase would delay the approach of equilibrium. Therefore, changes in equilibrium concentrations caused by changes in ventilation rate would occur most rapidly for slightly soluble species, typified by hydrogen.

Equation (6-6) also applies for cases where the initial ($t=0$) concentration is not zero, but a finite value, C_0 . For $C_0 > 0$, t_{90} is the time required for concentration to reach 90% of the change between C_0 and the maximum C. For example, if $C_0 = 0.5$ units and $C_{max} = 1$ unit, the time to achieve 90% of the change $[(1-0.5)(0.90) = 0.45$ units, i.e., a concentration of $0.5 + 0.45 = 0.95$ units] is correctly predicted by Equation (6-6).

The numerical value of Q_3 , the ventilation flow rate, can be estimated for several cases. For cases where the driving force for ventilation is the result of changes in atmospheric pressure, the daily variation amounts to approximately 0.45%. This value represents a yearly average based on hourly atmospheric pressure readings made at the Hanford Weather Station (Crippen 1993). The average daily volume exchange for tank C-103 is

$$Q_3 = \frac{0.0045}{(\text{day})} \times 2,550 \text{ m}^3 = 11.5 \text{ m}^3/\text{day}$$

or 0.48 m^3/h . The rate of radiolytic gas generation, which adds to ventilation rate, has been neglected because its contribution is typically less than 1% for cases where the combustible species concentrations are less than 25% of the LFL.

Using this ventilation rate, the value of t_{90} for slightly soluble species ($V_g \gg HV_l$) is, from Equation (6-6).

$$t_{90} = \frac{2.3(2,550)}{11.5} = 511 \text{ days}$$

Thus, based on this ventilation rate, roughly 1.4 years would be required to accomplish 90% of a change in equilibrium concentrations if instrument purge air flow was terminated at time zero, and if ventilation flow was driven entirely by atmospheric pressure changes.

Another source of ventilation air is purge air used in FIC level measuring gauges. Tank farm data sheets indicate that purge rates of 50 ft³/h (1.4 m³/h) are used in tank C-103 and C-102. No purge air is used in tank C-101 because C-101 is not equipped with a FIC gauge that requires an air purge. This flow rate is larger than the average caused by atmospheric pressure fluctuations and would have to be considered in interpreting one-time measurements of combustible gas species produced by first order kinetics. The value of t_{90} , as defined in Equation (6-6), is inversely proportional to Q_3 . Adding ventilation rates due to atmospheric pressure fluctuations and purge air (0.48 m³/h + 1.4 m³/h)(24 h/day) = 45 m³/day the value of t_{90} is calculated to be 130 days.

Buoyancy-induced air flows through leak paths and filtered vents can also cause headspace air ventilation. Claybrook and Burke (1991) analyzed naturally convected air flows in tanks C-103, -102, and -101 and estimated the average outflow from tank C-103 to be 0.007 lb/sec. Converted to volumetric flow rate, this mass flow rate amounts to 250 m³/day. This flow rate is significantly higher than flows caused by instrument purge air and breathing in response to atmospheric pressure fluctuations. While this convective flow rate would not be applicable under present conditions (the vent valve is closed and obvious leak paths have been sealed), it is referenced here to note that actual ventilation rates may be higher than computed from atmospheric breathing and instrument purge air alone.

Another case of interest involves the hookup of the three tanks in series as depicted in Figure 6-2. Vent valves on tanks C-101 and C-103 are currently closed, and the vent valve for tank C-102 is open. Tanks C-101 and C-103 are ventilated through tank C-102. Instrument air (1.4 m³/h) continuously purges the housing of the automatic level gauge and enters the headspace air of tanks C-103 and C-102. For this case, three simultaneous differential equations [similar to Equation (6-4)] may be written to describe the concentration of an airborne specie produced at a constant rate by radiolysis. These equations are not easily solvable in closed form but can be numerically solved. Results of one case in which sorption by liquids was neglected ($V_L H < < V_g$) are listed in Table 6-1.

Table 6-1. Predicted Buildup of Radiolytic Species in Tanks C-101, C-102^a, and C-103^a.

Time, days	Normalized concentration ^b		
	Tank C-101	Tank C-102	Tank C-103
1	0.01	0.02	0.02
10	0.06	0.16	0.17
100	0.66	0.64	0.94
150	0.94	0.73	1.08
500	1.98	0.92	1.23
1000	2.28	0.95	1.24

^aInstrument air purge flow rate of 1.4 m³/h.

^bRatio of concentration to steady state concentration based on direct venting of tank C-103 to the atmosphere.

The following conclusions may be drawn from the calculated results presented in Table 6-1.

- The time required to reach 90% of the steady state concentration in tank C-103 is ~ 150 days.
- The steady-state concentration reached in tank C-103 is 1.24 times larger than would be the case if tank C-103 were vented directly to the atmosphere (see footnote b of Table 6-1).
- The steady-state concentration reached in tank C-101 is 1.85 times the value that applies to tank C-103.

Table 6-1 results apply for a case in which source rates S_1 , S_2 , and S_3 were assigned values in proportion to decay heat loads in each tank. Based on average headspace gas temperatures, decay heat loads for the three tanks were calculated using the method described by Crowe (et al 1993). Heat loads, and consequently radiolytic source rates expressed as ratios referenced to tank C-103 were estimated to be 0.40, 0.72, and 1.0 for tanks C-101, C-102, and C-103, respectively. Note that tank C-101 is calculated to have an equilibrium concentration level higher than tank C-103. This higher concentration is predicted because the ventilation rate for tank C-101 is lower (atmospheric breathing only) than for the other two tanks. Based on recent measurements in tank C-103 (hydrogen concentration \cong 2% LFL), the hydrogen concentration in tank C-101 is projected to be less than 4% LFL.

A second three-tank hookup case was analyzed to illustrate how steady-state concentrations in tank C-103 could be affected by vent valve settings. For this case, it was assumed that vent valves were closed on tanks C-102 and C-103 and that the vent valve on tank C-101 was open. The steady-state concentration in tank C-103 (for an instrument air purge flow rate of 1.4 m³/h in tanks C-103 and C-102) was computed to be 1.65 times higher than would have been the case if tank C-103 had been vented directly to the atmosphere. For this case, the concentration in tank C-101 decreases to a fraction of the C-103 value.

The transient buildup in concentration that could occur if the air purge were inadvertently terminated was analyzed for the case where source terms were assigned to each tank in proportion to the decay heat load, and where the time zero concentration corresponded to equilibrium for purge rates of 1.4 m³/h (50 ft³/h) in tanks C-102 and C-103, and zero purge in tank C-101. Results are shown in Table 6-2.

Table 6-2. Predicted Buildup of Radiolytic Species in Tanks C-101, C-102, and C-103 Following Assumed Termination of Purge Air.

Time, days	Normalized concentration*		
	Tank C-101	Tank C-102	Tank C-103
0	1.85	0.77	1.00
20	1.86	0.94	1.26
40	1.88	1.06	1.52
60	1.91	1.15	1.76
80	1.94	1.22	1.98
100	1.98	1.28	2.19
200	2.18	1.52	3.07
1000	3.25	2.28	5.31
Equil	3.49	2.40	5.59

*Ratio of concentration to initial steady-state concentration in tank C-103.

Two important conclusions that may be drawn from the data of Table 6-2 are:

- Termination of purge air could cause radiolytic species to increase in concentration in tank C-103 by a factor of ~5.6.
- The buildup rate is quite slow. A doubling of the concentration of radiolytic species in tank C-103 (the tank predicted to be most affected by purge-air termination) would require approximately 80 days.

The following conclusions summarize the findings related to the flammable gas species which enter headspace air at a constant rate.

1. The time required to reach steady state concentrations of flammable species produced at a constant rate is hundreds of days. Thus the interpretation of sample data should account for recent changes in ventilation flow rates and pathways.
2. Venting of tank C-103 through other tanks (C-102 and/or C-101) causes steady state concentrations of combustible species (of radiolytic origin) to be higher than they would be if tank C-103 were vented directly to the atmosphere. The effect is not important for FIC purge rates currently used in tank C-102 and C-103.

3. Termination of purge-air flow could cause the concentration of radiolytic gases to increase, but the buildup takes place slowly.

6.1.2.2 Volatilization of Organic Liquid. Organic liquids in contact with headspace air exert a vapor pressure and this vapor would add to flammable species produced by other mechanisms. For a specific volatile liquid specie, the equilibrium concentration in the gas may be related to its mole fraction in the liquid using Henry's law:

$$C = HX \quad (6-7)$$

where:

C = Vapor concentration, mole/m³,
 H = Henry's law coefficient, moles/m³ mole fraction,
 X = Mole fraction of specie in liquid.

At the surface, the rate of evaporation may be expressed as the product:

$$\text{Evap. Rate} = kA(C_i - C_b) \quad (6-8)$$

where:

k = Mass transfer coefficient, m/h,
 A = Interfacial area, m²,
 C_i = Conc. at surface, moles/m³,
 C_b = Bulk conc. in gas, moles/m³.

The variation of concentration in headspace gas with time was modeled using Equation (6-8) to quantify the source term. Two hypothetical cases were considered: tank C-103 vented directly to the atmosphere, and tanks C-103 and C-101 vented to tank C-102, with tank C-102 vented to the atmosphere (the current arrangement). Using a derivation procedure similar to the one described for Equation (6-5), the variation of concentration with time, for the first case, is derived to be:

$$\frac{C}{C_i} = \frac{kA}{Q + kA} \left[1 - \exp - \left(\frac{Q + kA}{V} \right) t \right] \quad (6-9)$$

where:

- C = Concentration of component in bulk gas, mole/m³
- C_i = Concentration of component at interface, mole/m³
- Q = Ventilation flow rate, m³/h
- V = Volume of headspace, m³
- t = Time from when C = 0, h.

Key assumptions inherent in Equation (6-9) are the following.

- The bulk gas contained no volatile material (C = 0) at time = 0.
- C_i, k, A, and Q are constants.
- Bulk gas is well mixed.

Inspection of Equation (6-9) shows that for long times, C/C_i approaches the ratio kA/(Q + kA) as a maximum value. The time required to reach 90% of this value is given by:

$$t_{90} = 2.3 V / (Q + kA). \quad (6-10)$$

To quantify t₉₀ = for tank C-103, a value of k was estimated for n-tetradecane to be 1.9 m/h (6.2 ft/h) using the Chilton-Colburn analogy (Sherwood et al. 1975). Thus from Equation (6-10)

$$t_{90} = \frac{2.3(2,550 \text{ m}^3)}{(1.4 + 0.48) \frac{\text{m}^3}{\text{h}} + 1.9 \frac{\text{m}}{\text{h}} \times 411 \text{ m}^2} = 7.5 \text{ h.}$$

This time is short compared to the value estimated for radiolytically produced species (~ 150 days) and indicates that flammable constituents formed by evaporation from the liquid would quickly come to equilibrium.

A second case, in which tanks C-101 and C-103 are vented through tank C-102, was analyzed by numerically solving the three simultaneous differential equations that describe the buildup in airborne concentration with time. Results from this analysis are described as follows:

- The concentration of evaporable species in headspace air in tank C-103 increased from 0 (assumed concentration at time 0) to 90% of the equilibrium concentration in 7.5 hr.

- The concentration of the evaporable species in headspace air in tank C-103 increased to greater than 99% of equilibrium (saturation) concentration within a few days.
- The concentration of the evaporable species in headspace air in tanks C-101 and C-102 required hundreds of days to reach a maximum. The maximum concentration reached in these two tanks varied from 26% (0 instrument air flow rate) to 40% (1.4 m³/h instrument air flow rate into tanks C-103 and C-102) of the equilibrium concentration in tank C-103 headspace air.

The most important conclusion from this evaluation of the transient buildup of evaporable species is that volatile species of organics in the liquid will be present in the air in tank C-103 in concentrations close to the equilibrium level at all times. An exception would be for times when forced ventilation at relatively high flow rates was imposed. The forced ventilation case was not analyzed.

6.1.2.3 Flammable Aerosols. As discussed in Section 5.6.1, no visible aerosol was present in the bulk headspace air volume during a December 1993 sampling event. This observation is in contrast to earlier reports (Carothers 1993, Huckaby and Estey 1992) in which a fog had been observed. As noted in Section 5.4, headspace air temperatures undergo seasonal oscillations that may affect fog formation during part of the temperature cycle.

The earlier reports of fog have prompted speculation that organic and water vapors, volatilized from the organic liquid, could condense within the headspace, forming an aerosol which would represent a combustible specie. Attempts to explain the results of air samples now believed to be invalid (Huckaby 1994a), prompted Trent (1990) to postulate that an aerosol composed of NPH was the main contributor to combustible species in headspace air. An analysis of aerosol formation by condensation of vapors is presented in this report section.

Finely divided combustible materials in solid or liquid form can, under restrictive conditions, support a combustion wave. In general, high concentrations (by aerosol standards) of combustible materials in a finely divided (< 10 μm) state must be present.

For the present problem, work described by Zabetakis (1965) is germane. References cited by Zabetakis indicate that for fine mists (particle sizes below 10 microns) the combustible concentration at the lower limit is about the same as that in uniform vapor-air mixtures. In some cases, for larger drops and upward flame propagation, the lower limit appears to decrease due to drops falling toward the flame front. Data for kerosene (similar to NPH) presented by Zabetakis indicate that drops smaller than 10 μm diameter have the same LFL as vapor when expressed as mass concentration (~ 48 g/m³). For drops larger than 60 μm diameter, the LFL increases. As will be shown, aerosols present in the headspace of

Tank C-103 are expected to be smaller than 10 μm diameter. Therefore, their contribution to the flammability characteristics of the atmosphere is expected to be similar to that of vapor.

This report section addresses the following tasks:

- Describe how aerosols could form
- Predict maximum concentration in Tank C-103 headspace
- Compare predictions with available data
- Quantify flammability contribution of aerosols.

OBSERVATIONS OF FOG IN TANK C-103

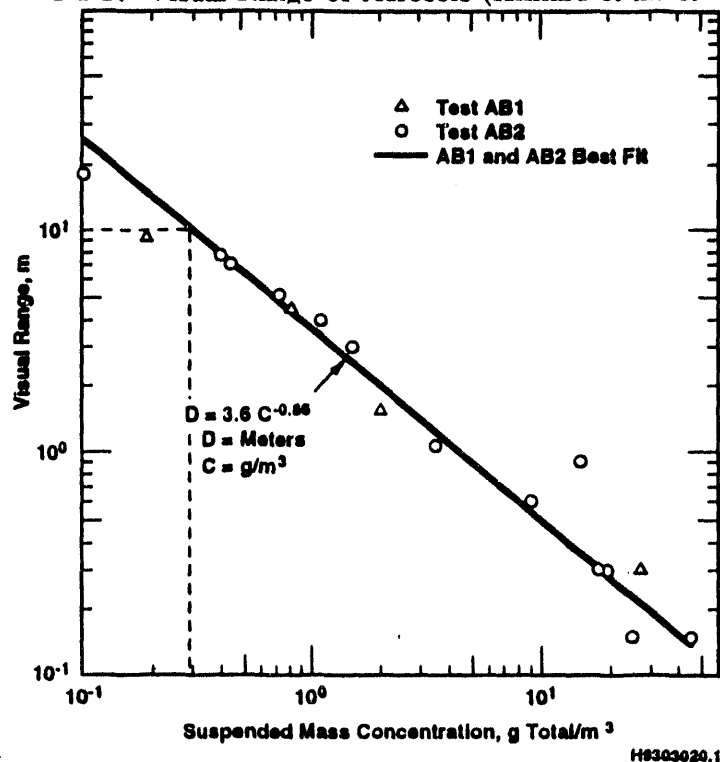
Visual inspections of the headspace atmosphere provides a means for making rough estimates of aerosol mass concentration. The following discussion applies to observations made several years ago. Operations personnel have observed a fog or haze that interfered with visibility and photography. According to Huckaby and Estey (1992) the surface of the waste approximately 10.1 m (33 ft) below the riser opening, was visible through the fog.

The mass concentration of the fog can be estimated by comparing this assumed visual range with visual ranges measured for known concentrations. Hilliard et al. (1979) correlated visual range with suspended mass concentration for sodium fire aerosols. As shown in Figure 6-3, similar results were obtained for both a dry aerosol (test AB1) and an aerosol composed of solution droplets (test AB2). For a visual range of 33 ft (10.1 m) an aerosol density of approximately 0.3 g/m^3 is indicated by the best fit line in the figure. This aerosol concentration (0.3 g/m^3) is similar to a value (0.2 g/m^3) estimated from a visibility-concentration algorithm presented by Hinds (1985).

The observed visual range provides a rough upper limit estimate of suspended concentration but sheds no light on particle composition. If the fog were composed of water drops, flammability would be retarded. If, on the other hand, the fog were composed of organic liquid, the aerosol would add to the flammable species concentration.

Recent sampling activities in tank C-103 have allowed visual inspection of headspace air. No observable aerosol was present in the tank when organic liquid samples were taken in December 1993 (Huckaby 1994a). It is likely that current tank conditions are less favorable for aerosol formation than conditions in former years. Changes which would diminish organic aerosol formation rates are (1) the tank heat load is lower and present because of radioactive decay, and (2) the more volatile organics have been depleted by the purging of headspace air with fresh air (instrument air, natural "breathing", and forced ventilation).

Figure 6-3. Visual Range of Aerosols (Hilliard et al. 1979).



EVAPORATION/CONDENSATION MECHANISM FOR AEROSOL FORMATION

Aerosols can be formed from organic materials in the floating liquid by the following processes.

1. Organics volatilize from the liquid into the gas phase at the gas/liquid interface. The layer of air at the interface becomes saturated with organic vapors.
2. The radioactive decay heat generated in the waste [approximately 5.3 kw (18,000 Btu/h)] warms the vapor-rich air and causes it to rise.
3. Because the temperature at higher elevations in the dome space is slightly cooler than at the interface, the vapor-air mixture is cooled below its dew point. This causes condensation on nuclei already present in the air.
4. Steady-state aerosol concentration is attained when the depletion rate (settling, plateout) equals the production rate by condensation.

In addressing the mode of aerosol formation, it must be recognized that the few degrees of cooling [approximately 2.2 °C (4 °F)] the air experiences as it is convected upward from the liquid surface does not allow sufficient supersaturation for homogeneous nucleation to occur

(Fletcher 1966). Aerosols could form only on pre-existing nuclei (heterogenous nucleation). Adequate nucleation sites are expected to be present in the dome space. Air brought in by tank breathing, natural convection and the air purge would introduce nuclei (airborne particles). Ionization of organic molecules by the radiation field in the headspace generates additional condensation nuclei (Megaw and Wiffen 1961). Therefore, organic vapors are expected to condense as aerosols whenever they become slightly supersaturated by the cooling of an air parcel convected away from the warm liquid surface toward the tank dome and exposed walls.

ESTIMATE OF MAXIMUM AEROSOL CONCENTRATION

A conservative estimate of maximum aerosol concentration in the headspace of tank C-103 that could result from the condensation of organic vapors originating from the liquid was made as follows.

1. It was assumed that organic aerosols were present and that the air was everywhere saturated with organic vapor.
2. The evaporation rate of organic vapor from the surface was computed using a concentration driving force that was consistent with the saturation assumption stated above.
3. A conservatively small rate of condensation on the tank surfaces was calculated and subtracted from the evaporation rate.
4. The remainder of the vapor evaporated from the pool surface was assumed to form small ($0.1 \mu\text{m}$ diameter) aerosol particles.
5. Particle concentration was computed as a function of time using the MAEROS Code (Gelbard 1982). The peak concentration corresponds to an equilibrium in which the depletion rate (fallout and plateout) is equal to the particle generation rate.

Details of the above-described aerosol analysis are provided in Appendix D. Key results are as follows.

- The maximum concentration attained for a best-estimate aerosol generation rate (1.2 mg/s) was predicted to be 0.04 g/m^3 .
- The maximum concentration attained for a conservatively high aerosol generation rate (12 mg/s) was predicted to be 0.2 g/m^3 .
- The maximum concentration, 0.2 g/m^3 , predicted for the conservatively high aerosol generation rate amounts to 0.4% of the LFI for NPH.

Based on these results, it is concluded that NPH aerosols formed by condensation in tank C-103 do not represent a flammability hazard. Because the aerosol model uses conservative assumptions regarding generation rates, the results are expected to bound actual aerosol concentrations that may occur during any part of the annual temperature cycle in tank C-103.

6.2 COMBUSTION OF ORGANIC LIQUID AS A POOL FIRE

In this section phenomena associated with pool fires in closed tanks are evaluated to provide a technical basis for controls needed to prevent a pool fire in tank C-103.

6.2.1 Adiabatic Burn to Oxygen-Limit Extinguishment

To put pool fire consequences into perspective, adiabatic constant-volume burns to the oxygen extinguishment limit were analyzed. Experiments on pool fires of kerosine-TBP mixtures in closed compartments have shown that the fire self-extinguishes when the oxygen concentration in the contained atmosphere falls to a level between 12% and 18% (Jordan and Lindner 1983; Malet et al. 1983). For the large-scale tests reported by Malet et al. (1983) the limiting O₂ concentration ranged from 13.5% to 13.75%. The oxygen extinguishment levels observed in these tests are consistent with oxygen deflagration limits cited by Lewis and Von Elbe (1987). The maximum safe oxygen limit for butane and higher hydrocarbons is provided by Lewis and Von Elbe (1987) as 12.1% and 14.5% for nitrogen and carbon dioxide as diluents respectively.

In applying these results to tank C-103, stoichiometry was based on n-dodecane as fuel:



The change in internal energy for this reaction was assumed to be the same as used earlier in this report for headspace deflagrations (Section 6.1.1), 1811 k Cal/g-mole. Initial conditions were assumed to be the same as for headspace deflagrations as listed on Figure 6-1. Results of the adiabatic, constant-volume burn calculations are listed in Table 6-3.

The data of Table 6-3 indicate that pressures of approximately 50 lb/in² (345 kPa) are predicted for O₂ extinguishment levels of 13% to 14%, the range found by Malet et al. (1983). These pressures are well above those the tank can safely withstand (Moore 1994).

Table 6-3. Pressure Rise Calculated for an Adiabatic, Constant-volume Burn of Dodecane in Air.

Assumed oxygen extinguishment limit (%)	Peak pressure kPa (lb/in ²)
12	416 (60.3)
13	370 (53.6)
14	321 (46.6)
15	272 (39.5)
16	226 (32.8)
17	173 (25.1)
18	121 (17.5)

Actual pressures caused by a pool fire in tank C-103 would be lower than those predicted by the adiabatic constant-volume calculation as a result of the following factors.

- The combustion energy would be lower than assumed because of incomplete combustion and the fact that TBP has a lower combustion energy than normal paraffin hydrocarbons.
- Heat transfer from combusted gas to the tank wall and internal structures could appreciably mitigate the pressure increase.
- Expansion work and loss of O₂ resulting from gas leakage during the burn could appreciably mitigate the pressure increase.

Two conclusions drawn from the adiabatic constant-volume burn calculations are:

1. Pressure generated by pool fires could pose a threat to tank structural integrity and, therefore, pool fires may pose a significant hazard.
2. Realistic assessments of pool fire pressures need to account for key mitigating factors.

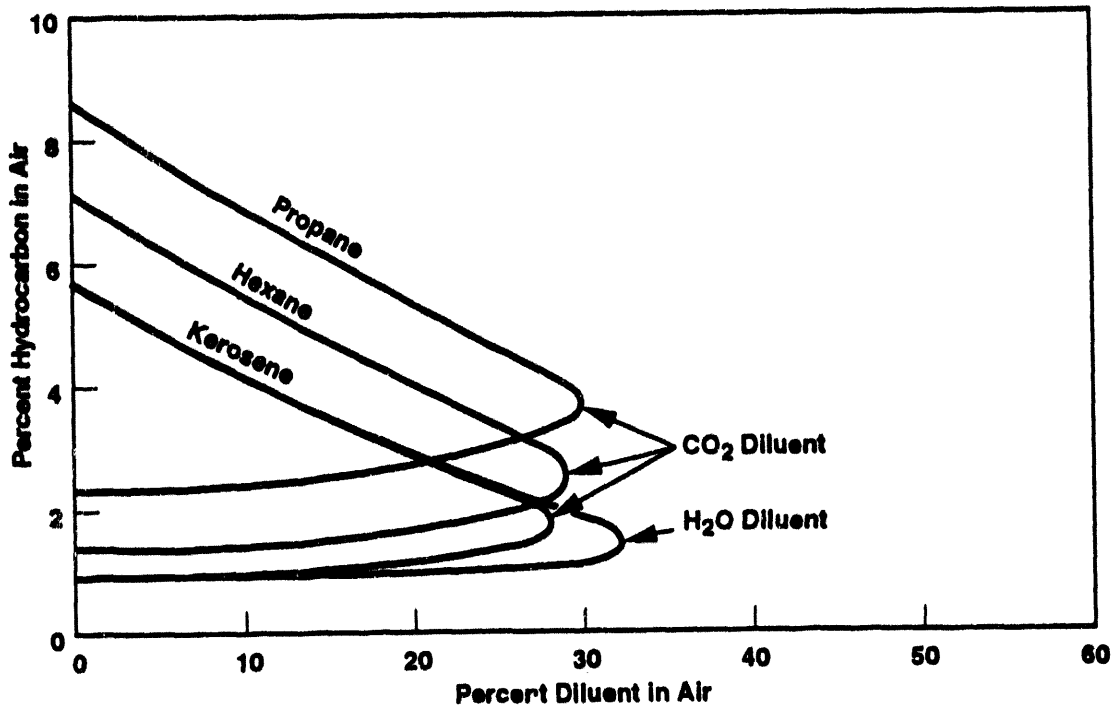
6.2.2 Pool Burning Phenomena

Flames above burning pools originate from a gas phase combustion in a zone above the liquid. The flame persists as long as the flame transfers enough heat to the surface of the liquid to produce vapor in flammable concentration in a mixing zone where vapor and oxygen react. Phenomena that govern ignition, flame spread rates, and burning rates are evaluated in the following sections.

6.2.2.1 Potential for Inerting by Water Vapor. Liquid fuels that contain water will not support a flame if the vapor evolved at the air-liquid interface contains more than approximately 30% water. The reason is that diluents in fuel-air mixtures cause a narrowing of flammability limits (Lewis and Von Elbe 1987). As the diluent concentration is increased, the upper and lower flammability limits converge to a single point. For still higher diluent concentrations, the mixture is not flammable (i.e., will not support a combustion wave). This well-known behavior is illustrated in Figure 6-4 (Burger 1956) where data for kerosene (a mixture of normal hydrocarbons similar to NPH) is presented. As indicated in Figure 6-4, kerosene is inerted when water vapor amounts to more than 33% by volume.

The inerting water vapor can originate either from the fuel or be present in the ambient atmosphere. As an example, if a tank contained water vapor in equilibrium with liquid water at 161 °F (72 °C), the atmosphere would contain 33% water (1 atm. total pressure) and pool burning would be impossible. Alternatively, if the vapor pressure of water over the liquid fuel was 4.8 lb/in² (33 KPa) or higher at the flashpoint temperature of dry fuel, the vapor evolved from the liquid into the mixing zone would be inerted by water vapor, and the pool would not burn.

Figure 6-4. Flammability Limits for Fuel-Air-Diluent Mixtures (Burger 1956).



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The fact that the organic liquid in tank C-103 is floating on water has the following implications with regard to pool fires and headspace deflagrations.

1. The flashpoint of the organic liquid ($>96\text{ }^{\circ}\text{C}$) is higher than the temperature ($72\text{ }^{\circ}\text{C}$) where water vapor would inert headspace air. Therefore, neither headspace deflagrations nor pool fires would be possible as a result of a global heating process that caused underlying water to closely follow the temperature of the organic liquid, and where water vapor equilibrium in headspace air was closely achieved.
2. The water content of the organic liquid, measured to be 1.3 wt% by Pool and Bean (1994), appears to be too low to inert headspace air. Therefore, water dissolved in the organic liquid would not prevent pool fires for postulated transient heating processes that caused local heating of the organic liquid without also heating the underlying water.
3. A pool fire, if assumed to be initiated, would heat underlying water, causing water vapor to enter headspace air. The increase in water vapor concentration in headspace air would aid self-extinguishment by reducing oxygen concentration as well as serving as an inert diluent.

6.2.2.2 Ignition of a Pool Fire. The ignition of flammable liquid requires that local regions, at least, be heated above the flashpoint. The flashpoint is the temperature at which vapor concentrations, in closed containers, are at the LFL. An ignition source applied to the vapor at the flashpoint will cause the vapor to "flash" but the liquid will not burn at this temperature because the rate of evaporation of fuel is too low to support a steady flame. A higher liquid temperature, called the "fire point" is required for the fire to be self-sustaining (Thorne 1983). Data presented by Thorne (1983) for five liquid fuels show fire points to be $15\text{ }^{\circ}\text{C}$ to $47\text{ }^{\circ}\text{C}$ higher than the flashpoint, suggesting that the initiation of a pool fire in tank C-103 would require that the organic liquid be heated (locally) more than $10\text{ }^{\circ}\text{C}$ above its flashpoint.

The evaporation of more volatile components from the NPH-TBP liquid in tank C-103 has caused the flashpoint to increase with time. Data on flashpoints of newly prepared NPH-TBP mixtures (Pool and Bean 1994) are presented in Table 6-4 to illustrate the effect.

Based on the flashpoint of fresh extractant ($101\text{ }^{\circ}\text{C}$ for a 30% TBP mixture) and the measured flashpoint ($118\text{ }^{\circ}\text{C}$) of liquid presently in tank C-103, the selective evaporation of volatile components has increased the flashpoint by an estimated $17\text{ }^{\circ}\text{C}$ ($31\text{ }^{\circ}\text{F}$).

While experience with open pools (Malet et al. 1983, Sutter et al. 1974) shows they are difficult to ignite if the liquid is substantially cooler than the flashpoint, the presence of a wick makes ignition relatively easy. In everyday experience one can light a candle, but a cylinder of wax without the wick cannot be ignited at room temperature. While an examination of photographs of the surface of the pool in tank C-103 indicates that wicks are

Table 6-4. Flashpoints of NPH-TBP Mixtures
(Pool and Bean 1994).

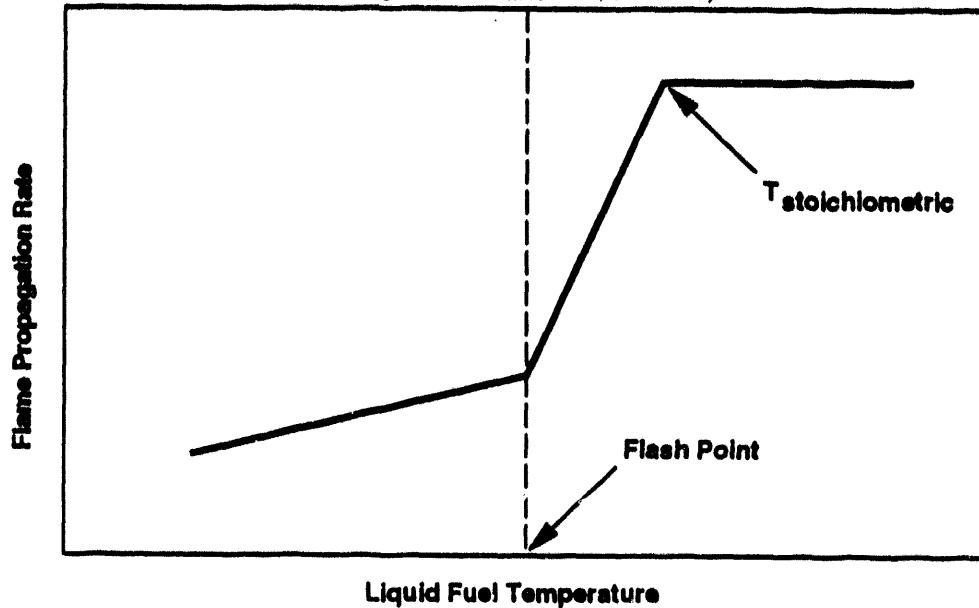
Percent TBP by volume	Flashpoint °C
0	87
10	94
20	97
30	101
40	104
50	106
60	112
70	119
80	126
100	181

not present, it is difficult to rule out altogether the existence of a solid at the air interface which could act as a wick. If present (and assumed to be lit) then a key question would be fire spreading rate discussed in the next section.

6.2.2.3 Pool Fire Spread Rates. The rate at which a local flame spreads is important in determining the peak pressure generated by a pool fire in a closed tank. If a small fire (few square feet of area) were stabilized by a wick (protruding saltcake or floating debris) but did not spread, then heat transfer and expansion work would limit the pressure rise to minimal levels. For this case the fire would burn to O_2 extinguishment levels and the incident would be self-terminating with minimal consequences. At the other extreme, the whole area of the pool could be inflamed and peak pressures could be comparable to the values for adiabatic burns.

Currently, no generally accepted model or correlation exists for easy use in predicting flame spreading rates. In a review of the topic, Quintiere (1988) notes that for liquid temperatures below the flashpoint, liquid phase effects control and for temperatures above the flashpoint, gas phase effects control. This is illustrated graphically in Figure 6-5. As indicated, the spread rate is low and increases with temperature until the liquid is heated to the flashpoint. Studies of flame spreading rates (Glassman and Dryer 1980, Akita 1973) indicate that liquid properties (surface tension, viscosity) are of prime importance in this low temperature region. Above the flashpoint the spread rate increases to a maximum that is controlled by flame speeds for premixed vapors. The maximum spread velocity was stated by Glassman and Dryer (1980) to be four to five times the laminar burn velocity and is attained when liquid temperature is high enough to generate vapors which form a stoichiometric mixture above the pool.

Figure 6-5. Effect of Liquid Temperature on Flame Spread Rate (Glassman and Dryer 1980).



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Based on this review of pool fire spread rates, a pool fire in tank C-103 (assuming initiation) would spread at a relatively low rate. Reasons for this assessment are as follows.

- Temperatures higher than the flashpoint, where spread rates increase rapidly (see Figure 6-5), are not applicable to tank C-103. The reason is that the closed volume in the tank would become water inerted (see Section 6.2.2.1) at temperatures of ~ 72 °C. Compared to the measured flashpoint (118 °C) the liquid would be subcooled by ~ 46 °C or more for pool temperatures where fires are possible.
- Because the maximum bulk liquid temperature where fire is possible is well below the flashpoint, spread rates of the order of 1 cm/s, the value observed by Glassman and Dryer (1980) for kerosene (subcooled by approximately 30 °C compared to its flashpoint) would be expected to apply to tank C-103. Therefore, a spread rate of ~ 1 cm/s or less would be expected apply to tank C-103.

6.2.2.4 Maximum Burning Rate. Burning rates for liquid pools, expressed as $\text{kg/m}^2 \text{ min}$, increase with pool size to an asymptotic value for large pools. Babrauskas (1988) provides a correlating equation of the form:

$$\dot{m} = \dot{m}_\infty (1 - e^{-kBD}) \quad (6-11)$$

where:

- \dot{m} = Burn rate, kg/m² min
- \dot{m}_∞ = Burn rate for a large pool
- kB = A constant, m⁻¹
- D = Pool diameter, m.

For kerosene the kB product is given by Babrauskas (1988) as 3.5 m⁻¹, and based on Equation [6.11], \dot{m} reaches 95% of the maximum value for a pool 0.9 m in diameter. This projection, based on experimental data, indicates that data from pools roughly 1 m in diameter would apply reasonably to a waste tank.

Tests of burning TBP-NPH mixtures in closed vessels showed that burning rates were 40% to 50% lower than for fires in the open air (Jordan and Lindner 1983). Mean combustion rates for enclosed large pools were measured to be approximately 1.2 kg/m² min of organic liquid (Jordan and Lindner 1983).

6.2.3 Realistic Estimates of Tank Pressurization Resulting from Postulated Pool Fires

Pressures generated by postulated pool fires in tank C-103 are estimated by means of a realistic model. The objective is to help put the pool fire hazard into perspective. Key variables are assigned best-estimate values or are treated parametrically. The predictive model embodies the following key assumptions.

- Burning rate is assigned a value of 1.2 kg/m² min, a value determined from the experiments reported by Jordan and Linder (1983).
- Flame spread rate is treated parametrically.
- Headspace air is assumed to be well mixed.
- Heat loss from headspace air to tank walls by radiation and convection is accounted for.
- The fire is assumed to self-extinguish when the oxygen concentration falls to 13%.
- Gas venting rate was treated parametrically by treating vent paths as circular orifices of arbitrary diameter.
- The thermodynamic impact of gas expansion (inside the tank) due to venting was modeled as a reversible expansion.

- Combustion energy was calculated as a weighted average for TBP and NPH.
- Evaporation of water during the fire was neglected.

Results of these calculations help assess the significance of the pool fire hazard. A specific objective of the analysis was to identify fire parameters for which a pool fire would threaten tank structural integrity. If a realistic set of fire parameters leads to calculated pressures that would threaten tank integrity, then it may be concluded that heat transfer and gas outflow effects would be unlikely to diminish burn pressures sufficiently (as compared to adiabatic, constant volume calculations exhibited in Table 6-3) to prevent tank damage as a result of a postulated pool fire.

6.2.3.1 Stationary Small Fire. For this case, a wick-stabilized flame having an area of 1 ft² (0.093 m²) is postulated. The combustion energy was computed for TBP and NPH using heat of reaction data measured in a bomb calorimeter for NPH and TBP (Lee 1974):

$$\Delta H = -[0.67(12,380) + 0.33(18,920)] = -14,540 \text{ Btu/lb } (-33.8 \text{ MJ/kg})$$

The mass fraction of TBP was taken as 0.67 (Pool and Bean 1994), the combustion energies (12,380 Btu/lb [28.8 MJ/kg] for TBP and 18,920 Btu/lb [44 MJ/kg] for NPH) were taken from the report of Lee (1974). The outflow of headspace gas was computed for an orifice diameter of 4 in. using a flow coefficient of 0.6. Results are as follows:

- A peak overpressure of 0.044 lb/in² gauge (0.3 kPa) was attained shortly after burn initiation
- The fire goes out at 9 hours after initiation
- 127 lb (57 kg) of organic liquid (stoichiometry based on C₁₂H₂₆) is consumed.

The low pressures generated by such a fire would not structurally damage the tank. Smoke produced by the fire could plug the vent filter, resulting a slight pressurization (calculated to be 1.0 lb/in² gauge [7 kPa] or less) of the tank. Smoke escaping from the tank would carry a small quantity of radioactive particulate material into the atmosphere.

6.2.3.2 Spread Rate Controlled by Liquid Phase. For this case, the fire was assumed to spread from an initial region (a circle having an area of 1 ft² [0.093 m²]) at a velocity of

1.0 cm/sec. This velocity was cited as a realistic estimate in Section 6.2.2.3. The initial pool was assumed to be centered in the tank. Time for engulfment of the whole tank is:

$$\text{Time for spread} = 37.5 \text{ ft} \times 30.5 \frac{\text{cm}}{\text{ft}} \times \frac{1 \text{ sec}}{1.0 \text{ cm}} = 1144 \text{ sec}$$

The outflow of headspace gas was computed for an orifice diameter of 4 in. using a flow coefficient of 0.6.

Results of the calculation for this case are:

- The fire burned to the oxygen-extinguishment limit in 290 seconds
- The peak pressure calculated was 16.7 lb/in² gauge (115 KPa) and occurred at the end of the burn.

The calculated tank internal pressure for this case, 16.7 lb/in² (115 kPa), is higher than the estimated pressure [14 lb/in² (96.5 kPa)] that the tank can safely contain (Moore 1994). Based on this higher-than-safe pressure that is calculated for a relatively slow fire spread rate, it is concluded that a pool fire in tank C-103, if initiated, could result in structural damage to the tank. Operational controls that prevent pool fire initiation appear to be needed for safe interim storage of the organic liquid.

6.2.4 Discussion of Pool Fire Initiation

As discussed in Section 6.2.2.2, a pool fire in tank C-103 is possible only if the global temperature of the aqueous-organic supernatant liquid is lower than ~72 °C. Water vapor would inert headspace air for higher temperatures. This temperature is well below the measured flashpoint, 118 ± 2 °C (Table 5-1), so the initiation of a pool fire in tank C-103 requires both the local heating of organic liquid to above the flashpoint, and the introduction of an ignition source into a flammable air fuel mixture immediately above the locally heated liquid.

Two key criteria thus exist for determination of the potential for a pool fire to be ignited and to propagate across the tank C-103 organic layer. First, for the case of local pool heatup, how much energy is required to heat a portion of the pool above its fire point so that, if ignited, the local flame could propagate? Second, for the case of a wick-stabilized flame, how large a wick flame (a stable energy source provided by the flame) is similarly required?

A qualitative answer to these question is that heat input from the source to a local pool surface region exceeds the heat removal rate from this region, so that the region heats up to

its flashpoint, and the flame spreads across the region. The region is large enough that the heat evolved and radiated to adjacent portions of the pool in turn brings these portions above the pool flash point, whereupon ignition occurs, and the flame propagates.

This rationale has been employed to ignite surface fires on TBP-NPH pools (Malet et al. 1983). Malet's experiments pertinent to this issue employed 200 liters of 30% TBP and 70% NPH in a pool with a surface area of 4 m² and a depth of 5 cm. The tray holding the pool was placed in a closed vessel. The pool could be heated in bulk to a desired initial temperature, and it could also be heated in a small central region by an immersed resistor. This region was confined by a barrier to prevent convective heat losses to the rest of the pool. Two kW of power were input by this immersion heater. Ignition was accomplished by two to four 200 W electric arcs above the center.

These experiments are at a scale applicable to tank C-103 because the layer depth was 5 cm (2 in.) and the radial extent (greater than 100 cm) was large compared to depth; these experiments also employ pertinent materials. While wicks were not used per se, one important feature of a wick-stabilized flame is its power, which in part is available for heating the pool.

Therefore, Malet's experiments provide information directly applicable to the case of a heat source applied to the tank C-103 layer as opposed to a wick-stabilized flame. The energy requirement for a wick-stabilized flame to propagate may be similar, but this cannot be stated with certainty at this time.

According to (Malet et al. 1983), "In all cases [a] large amount of energy was necessary to start the combustion." Confinement of the local zone was a key feature of the heating technique, because without the barrier much of the input power would have been lost by convection in the pool radially away from the heaters. The large radial extent of Malet's experiments relative to the source size suggest applicability to tank C-103. A source in tank C-103 would necessarily be far greater than that of Malet's experiments because of radial losses (minimized by the confinement technique) and losses to the underlying supernate. Thus, for TBP-NPH pools, a heat source must produce a power output in great excess of 2 kW, probably of the order of 10 kW.

The necessary duration of an energy source was not directly stated by Malet (1983) but his wording implies a period on the order of minutes, perhaps about ten minutes, to achieve a large amount of energy. (A period on the order of a minute would have been trivial, while a period on the order of an hour would have complicated the experiment and is likely to have been mentioned). A 10-minute heating period at 2 kW is 1.2 MJ energy. A 1.2 MJ is roughly the amount of amount of energy required to heat up 2 kg of organic material to its boiling point, and partly evaporate some in the process. Such a mass corresponds to slightly over 2 liters of organic liquid, or 1% of Malet's total fluid volume of 200 liters, which is consistent with the volume expected in a confined portion of the pool.

It may be concluded that a total energy requirement of 1 MJ or greater was needed (Malet et al. 1983) to create a locally ignitable TBP-NPH region, and that the same or greater energy would be necessary in the case of tank C-103 due to the similarity in layer geometry. Extra energy is needed in the case of tank C-103 due to the lack of confinement, a higher flashpoint liquid, and the presence of the underlying aqueous supernate.

What kind of energy sources can produce the required levels of power and duration to initiate a pool fire in the tank C-103 organic layer? Resistive heating, sustained electric arc, a large burning object or torch flame, are possible sources. Energy generated by the source must be released just above or within the organic layer, and not to the underlying supernate. Any energy source in contact with the underlying supernate would transfer much of its energy to the water and not the organic layer.

The power used by Malet may also be compared with the output of a possible wick-stabilized flame. A typical candle produces a few watts to 10 watts. Conservatively speaking, the required source is two to three orders of magnitude larger than that of an everyday candle. More practically visualized, the equivalent of several hundred to a thousand ordinary candle wicks in close proximity are required for an equivalent source. Note that metal or plastic equipment would not provide a wick site, since a porous material is required. The required wick corresponds qualitatively to a piece of flaming porous solid debris embedded in the organic layer. Thus, if the power requirement for a wick-stabilized flame is similar to that of some other heat source, a large wick would be required for a flame to propagate.

Dropping a flaming, non-floating object into the organic layer is not likely to initiate a pool fire. First, any dropped object would partly or completely penetrate the layer, simultaneously losing contact with the air (oxidizer) and coming into contact with relatively cool fluids -- thus, flames on the object would be quenched. Second, the energy imparted to the layer by the flames on the object would be rather low, since the transient contact time would be a second or less. Stored thermal energy in the object would be conducted out slowly after the initial quench. Only if the object were extremely buoyant, or dropped from a short distance, is it likely that it would both float and continue to burn.

6.2.5 Discussion of Condensate Film Fire Initiation

Organic vapors evolved into headspace air at the organic liquid-air interface could condense on cooler surfaces in the tank. Examples of cooler surfaces are the tank dome and equipment (cameras, illuminating lights, etc.) inserted into the tank atmosphere. Equipment normally would undergo a heat transient because ambient air normally is colder than headspace air. Surface films formed by condensation represent an additional liquid fire hazard that needs to be considered.

Two types of condensate films were evaluated:

1. Condensate film on tank wall
2. Condensate film on equipment.

Film thickness computed from laminar flow theory (Bird et al. 1960), using the condensation rates estimated in Appendix D, are small. For a vertical surface, a film thickness of 14 μm is predicted. A film of this thickness, composed of a high flashpoint liquid, would be difficult to ignite because it could lose heat very rapidly to the solid surface behind it.

Similar thicknesses are predicted for films which would form on cool equipment inserted into the warm headspace air. Based on a transient heatup time of 4 hours, an organic vapor concentration of 1 g/m^3 , and a mass transfer coefficient of 1.9 m/h (from Appendix D), an organic film thickness of 8.4 μm was predicted. An organic film of this thickness would be difficult to ignite because it would lose heat rapidly to the underlying material.

In the discussions above, water vapor has been neglected. The concentration of water vapor, if saturated at 40 °C, would amount to 52 g/m^3 . This is ~50 times higher than the mass concentration of organic vapor. Therefore liquid condensing on surfaces inside the tank would probably be mostly water. Organic condensate would likely be present as a very thin film on a water film, making ignition very improbable.

Based on the discussion above, it is concluded that fires involving organic condensate on tank wall or on equipment inserted into the tank atmosphere do not pose a credible hazard in tank C-103.

6.2.6 Conclusions Regarding Pool Fires in Tank C-103

- The current temperature of the organic liquid in tank C-103 (~40 °C) is approximately 80 °C below its measured flashpoint (118 ± 2 °C). The ignition of a pool fire would require the imposition of a local high energy source at the organic-air interface to heat the organic liquid to a temperature above its flashpoint and the simultaneous introduction of an igniter into the flammable organic-air mixture immediately above the heated liquid.
- The global heating of organic-aqueous supernatant liquid to temperatures greater than ~72 °C would likely cause the tank atmosphere to be inerted by water vapor, making pool fires and deflagrations in headspace air impossible. Therefore, only local heating/ignition sources could initiate a pool fire in tank C-103.
- A wick, if present, could lower the required energy for ignition as compared to an open pool. A review of photographs of the surface of the pool failed to identify the presence of wick-like materials in tank C-103.

- Peak pressures calculated for adiabatic, constant volume burns of a pool fire are approximately half the values calculated for a premixed deflagration because the pool fire self-extinguishes at an oxygen limit of approximately 13%. This self-extinguishment behavior does not eliminate the pool fire hazard because calculated peak pressures still exceed the structural capabilities of the tank.
- A wick-stabilized small fire (0.3 m dia.) would burn to extinction without generating an overpressure that would challenge tank structural integrity.
- A locally ignited pool fire that spread from its source and covered a significant area of the pool would likely cause overpressures that would challenge tank integrity. Therefore, the consequences of a pool fire can be best avoided by maintaining controls on tank operations that prevent the ignition of a pool fire.

6.3 ORGANIC-NITRATE/NITRITE REACTIONS

The potential for exothermic reactions in organic wastes has been studied since the 1970s. Beitel (1976a, 1976b, 1977) carried out tests with simulants and identified conditions (concentrations of reactants, moisture levels, and temperature) under which significant reactions could be observed.

More recently Fisher (1990) conducted a series of screening tests designed to identify organic concentration levels where dry wastes could undergo a deflagration if heated to above reaction threshold temperatures. These tests identified an organic carbon level, expressed as sodium acetate, of 10% as a criterion for gauging waste reactivity. Fisher (1990) then examined available waste composition data and identified seven single-shell tanks estimated to have 10% or more sodium acetate on a dry basis.

Tank C-103 was not among the seven tanks identified as having potentially reactive organic salt concentrations and based on the 10% acetate gauge would not pose a hazard on the basis of organic-nitrate/nitrite reactions. This issue is discussed in this report section using thermodynamic calculations to judge potential reactivity.

Currently, the sludge in tank C-103 is covered by aqueous supernatant liquid. The presence of the aqueous liquid makes it virtually impossible for an organic-nitrate/nitrite reaction to pose a significant hazard. This can be shown by energy balances where theoretical reaction energy is compared to the endotherm arising from the evaporation of water and the heating of solids to reaction threshold temperatures.

Supernatant liquid has been analyzed for organic carbon (Edrington 1991) and the concentration in two samples was reported as 7.44 and 7.46 g/l respectively (see Table C-2

of Appendix C) of total TOC. Nitrate and nitrite together added to 34.7 g/l. If it is assumed that the TOC is present as sodium acetate, a relatively energetic chemical form (Crippen 1991a), the reaction energy per liter of liquid is

$$7.45 \frac{\text{gC}}{\text{l}} \times \frac{1 \text{ mole C}}{12\text{g C}} \times 77 \frac{\text{Kcal}}{\text{mole C}} = 47.8 \frac{\text{Kcal}}{\text{l}}$$

The evaporation of 907 g of water in the liter of supernatant liquid requires an energy input of

$$0.907 \text{ kg } H_2O \times 540 \frac{\text{kcal}}{\text{kg}} = 490 \text{ kcal.}$$

Comparing these two energies shows that the reaction exotherm is far too small to evaporate water present and one can conclude that organic-nitrate/nitrite reactions pose no threat in the aqueous supernatant liquid.

Drainable liquid in sludge retrieved in core samples (see Table C-3 of Appendix C) had TOC levels of 7.37 g/l and 7.2 g/l for cores 1 and 2 (Weiss and Schull 1988).

These concentrations are similar to those in the supernatant liquid, and the energy balance described above shows that the organic-nitrate/nitrite reaction in drainable liquid poses no hazard.

Sludge solids separated from drainable liquid had measured TOC levels of 3.9 and 2.61 g/kg, respectively, for core samples 1 and 2. Drained solids had reported moisture contents of 37% and 41% respectively. The theoretical reaction energy per kg of drained sludge for core 1 (the sample with the highest TOC) is

$$3.9 \frac{\text{gC}}{\text{kg}} \times 77 \frac{\text{kcal}}{\text{mole C}} \times \frac{1 \text{ mole C}}{12\text{gC}} = 25.0 \frac{\text{kcal}}{\text{kg}}$$

The endotherm for moisture evaporation for one kg of drained sludge for core 1 is

$$0.37 \frac{\text{kg } H_2O}{\text{kg}} \times 540 \frac{\text{kcal}}{\text{kg } H_2O} = 200 \frac{\text{kcal}}{\text{kg}}$$

The endotherm computed above is much larger than the theoretical exotherm and it is evident that organic-nitrate/nitrite reactions do not pose a hazard for solids in the sludge.

Nonuniform distributions of decay heat in the wastes have been postulated as a means for drying out local regions and possibly creating "hot spots." The threat posed by postulated "hot spots" in sludge in tank C-103 appears to be minimal for the following two reasons.

1. The sludge is submerged beneath aqueous liquid.
2. Theoretical reaction energies appear to be too low to support a propagating reaction even in dry sludge.

Item 2 above is supported by an endotherm calculated for a temperature increase in dry waste solids from 65 °C to 200 °C (Babad and Turner 1993).

$$0.63 \frac{\text{kg solids}}{\text{kg sludge}} \times (200-65)^{\circ}\text{C} \times 0.31 \frac{\text{kcal}}{\text{kg solids } ^{\circ}\text{C}} = 26.4 \frac{\text{kcal}}{\text{kg sludge}}$$

The endotherm calculated for zero moisture is larger than the exotherm (26.4 vs 25.0) and one can conclude that a propagating reaction could not be sustained even in dry solids.

In summary, simple energy balances confirm that organic-nitrate/nitrite reactions do not pose a significant hazard for wastes currently in tank C-103.

7.0 ASSESSMENT OF HAZARDS FOR TANK OPERATIONS

Tank operations are evaluated in this section against the hazards discussed in Section 6.0. The objective is to identify how an operation could result in uncontrolled exothermic reactions. Based on this evaluation, controls required to prevent a hazard from causing an uncontrolled reaction will be formulated.

7.1 SUMMARY DESCRIPTION OF OPERATIONS AND HAZARDS FOR TANK 241-C-103

Table 7-1 summarizes an assessment of potential hazards related to tank intrusive operations proposed for tank 241-C-103. These operations are required, or could be required, to ensure the continued safe interim storage of the high-level radioactive waste stored in this single-shell tank. Proposed tank intrusive operations include the following:

- Liquid level monitoring
- Sludge level monitoring
- Temperature monitoring
- Still camera photography
- Video camera operation
- Portable exhauster operation
- Breather filter testing/maintenance
- Sorbent bed testing/maintenance
- Pit cover block removal/replacement
- Riser flange and gasket removal/replacement
- Riser modifications
- Waste sampling
- Inadvertent addition of high-level waste
- Small volume water additions
- Passive tank ventilation.

These proposed operations have been assessed against four potential hazards for both normal and operational upset conditions. The four potential hazards described in Section 3.4 are

- Deflagration of gases, vapors and aerosols in the tank's headspace (headspace deflagration)
- Ignition and combustion of the floating organic layer (organic pool fire)
- Organic - nitrate reaction within the floating organic layer.
- Organic - nitrate reaction within the sludge layer.

Table 7-1. Assessment of Hazards for Tank Intrusive Operations. (3 pages)

Tank Intrusive Operations ¹	Potential Hazards Normal Operations			Potential Hazards Operation Upsets				
	Headspace Deflagration	Organic Pool Fire	Organic-Nitrate Reaction		Headspace Deflagration	Organic Pool Fire	Organic-Nitrate Reaction	
			Organic Layer	Sludge Layer			Organic Layer	Sludge Layer
Liquid level monitoring - operation	N	N	X	X	N ²	N	X	X
Liquid level monitor - maintenance ²	C	C	X	X	C	C	X	X
Sludge level monitoring	C	C	X	X	C	C	X	X
Temperature monitoring - operation	X	X	X	X	N	X	X	X
Temperature monitor - maintenance	C ⁴	C	X	X	C ⁴	C	X	X
Still camera photography	C	C	X	X	C	C	X	X
Video camera - operation	C	N	X	X	C	C	X	X
Video camera - maintenance ²	C	C	X	X	C	C	X	X
Portable exhauster - operation	C	X	X	X	C	X	X	X
Portable exhauster - maintenance ²	C ⁴	X	X	X	C ⁴	X	X	X
Breather filter-testing/maintenance ²	C ⁴	X	X	X	C ⁴	X	X	X
Sorbent bed testing/maintenance ²	C ⁴	X	X	X	C ⁴	X	X	X
Pit cover block-removal/replacement	C	X	X	X	C	X	X	X
Riser flange and gasket - removal/replacement	C	C	X	X	C	C	X	X

Legend:

- X = Hazard not present
- N = No control required
- C = Control(s) preclude hazard
- A = Operation requires further analysis.

Table 7-1. Assessment of Hazards for Tank Intrusive Operations. (3 pages)

Tank Intrusive Operations ¹	Potential Hazards Normal Operations				Potential Hazards Operation Upsets			
	Headspace Deflagration	Organic Pool Fire	Organic-Nitrate Reaction		Headspace Deflagration	Organic Pool Fire	Organic-Nitrate Reaction	
			Organic Layer	Sludge Layer			Organic Layer	Sludge Layer
Riser modifications	C	C	X	X	C	C	X	X
Waste sampling - gases, vapors, aerosols	C	C	X	X	C	C	X	X
Waste sampling - liquids	C	C	X	X	C	C	X	X
Waste sampling - push-mode core	C	C	X	X	C	C	X	X
Addition of high-level waste from inadvertent leakage	X	X	X	X	C	X	X	X
Small volume water additions into the tank ²	X	X	X	X	X	X	X	X
Passive tank ventilation ⁴	C ¹⁰	X	X	X	C ¹¹	X	X	X
Liquid observation well (LOW)-installation/removal ¹²	A	A	A	A	A	A	A	A
Thermocouple tree - installation/removal ¹²	A	A	A	A	A	A	A	A
Transfer pump - installation/removal ¹²	A	A	A	A	A	A	A	A
Salt well screen - installation/rm.oval ¹²	A	A	A	A	A	A	A	A
Removal of floating organic layer from tank ¹²	A	A	A	A	A	A	A	A

Legend:

- X = Hazard not present
- N = No control required
- C = Control(s) preclude hazard
- A = Operation requires further analysis.

Table 7-1. Assessment of Hazards for Tank Intrusive Operations. (3 pages)

¹A non-intrusive operation is characterized by the presence of a boundary that physically separates the instrument, equipment, or process in question from the tank's waste contents (headspace gases, vapors and aerosols/liquids/solids). An intrusive operation is characterized by the absence of such a physical boundary.

²Includes, as appropriate:

- Instrument calibration, preventive maintenance, and repair
- Installation, removal, replacement, and modification of small-scale instruments, components, and equipment
- Installation, removal, replacement, and modification of above ground facility instruments, components, and equipment.

³Small volume waste additions into the tank to flush instruments, enter pits, decontaminate pits, conduct routine maintenance, pressure test transfer pipelines, flush transfer pipelines, dispose of rain water and snow-melt, and to flush for equipment removal and installation purposes.

⁴Considered to be an inherently non-intrusive operation, but requires controls to prevent an increase in the concentration of radiolytically generated gases.

⁵Potential off-normal condition: instrument air to liquid level monitor shut off, thereby decreasing the tank's passive ventilation rate and increasing the concentration of radiolytically generated gases.

⁶Thermocouples can be removed from and replaced in the tank's thermocouple tree non-intrusively under normal conditions.

⁷Potential off-normal condition: due to corrosion the steel barrier separating the thermocouple from the tank's waste contents fails, thereby creating a tank intrusive condition.

⁸Valved out of ventilation system for maintenance under normal condition.

⁹Potential off-normal condition: failure to valve out of ventilation system prior to maintenance.

¹⁰Tank C-103 is passively ventilated through a breather filter and sorbent bed (in series) and/or through tanks C-102 and C-101. Some passive ventilation occurs along the edges of pit cover blocks where (at points) the integrity of the cover block seals no longer exists.

¹¹Potential off-normal condition: all vents which permit the tank to passively ventilate are shut off, thereby increasing the concentration of radiolytically generated gases.

¹²This operation is not addressed in this safety analysis.

The results of the hazards assessment for each operation are indicated in Table 7-1 using the following legend:

- X = Hazards determined not to be present
- N = No controls required to ensure continued safe interim storage
- C = Control required to ensure continued safe interim storage
- A = Operation requires further safety analysis.

The hazards assessment for each operation is presented in Section 7.2.

Several operations that are non-intrusive have not been included in Table 7-1. These operations are also required, or could be required, to ensure the continued safe interim storage of the high-level radioactive waste stored in tank 241-C-103. Hazards similar to those presented in Table 7-1 are not postulated for these non-intrusive operations. This is because the non-intrusive operations in question are incapable of imparting sufficient energy to the tank's waste contents to create one of the hazards that have been addressed for intrusive tank operations. A non-intrusive operation is characterized by the presence of a boundary that physically separates the instrument, equipment, or process from the tank's waste contents (headspace gases, vapors and aerosols, liquids and solids). An intrusive operation is characterized by the absence of such a physical boundary. The non-intrusive operations include the following:

- Dome deflection surveys
- Liquid observation well (LOW) scans
- Dry well scans.

An authorization basis currently exists (the JCO) for conducting all operations listed in Table 7-1 with the exception of push-mode core sampling of the sludge solids in tank 241-C-103 (Carothers 1993). Operations for which an authorization basis currently exists are included in this safety analysis for completeness. Push-mode core sampling is scheduled to be conducted in tank 241-C-103 during May 1994.

This safety analysis does not address the following operations:

- Liquid observation well (LOW) installation/removal
- Thermocouple tree installation/removal
- Transfer pump installation/removal
- Saltwell screen installation/removal
- Removal of the floating organic layer from the tank.

No plans currently exist for liquid observation well or thermocouple tree installation or removal. Operations involving transfer pump and/or saltwell screen installation or removal will require completing safety analyses before implementation.

Removal of the floating organic layer from tank 241-C-103 is scheduled to be completed by March 1995. This operation is not addressed in this safety analysis because the procedure and equipment to be employed have not been sufficiently well defined at this point in time. The conduct of this operation will require the completion of safety analyses before its implementation.

7.2 SUMMARY OF HAZARDS ASSESSMENT

Potential hazards discussed previously will be reviewed here so that the operations on tank C-103, as identified in Table 7-1, can be evaluated for possible accident initiators. A two-step approach will be followed. The hazards will be examined to establish criteria that may be used to either dismiss a hazard or identify a control applicable to many operations. Each of the four hazards will be addressed in this manner for normal operations and for operational upsets. As will be shown, several hazards can be dismissed for most or all operations; likewise, a specified control adequately addresses a hazard for most or all operations. Operations and hazards that require specific controls will be identified and the appropriate control will be described.

7.2.1 Summary of Headspace Deflagration Hazard

A deflagration in headspace air is possible only if the concentration of combustible species is higher than the LFL and an igniter is present. This study assumes that an igniter for an air-fuel mixture cannot be ruled out, and that in order to preclude headspace deflagrations, the fuel concentration must be maintained below the LFL.

The following key assumptions are embodied in the evaluation of this hazard.

- Combustible species include:
 - Vapors volatilized from the organic liquid
 - Organic aerosols
 - Gases and vapors produced by radiolysis and other chemical reactions
- The acceptable concentration of combustible species is 25% of the LFL
- Headspace air is well-mixed
- Episodic gas releases are unimportant from a flammability standpoint for tank C-103.

7.2.1.1 Volatilization of Organic Liquid. Samples of headspace air and the organic liquid (Section 5.0) show that under current conditions, alkanes and TBP vapor concentrations add to less than 4% of the LFL. Analysis of mass transfer between the pool and headspace air

(Section 6.1.2) showed that equilibrium concentrations are achieved in a period of hours. Therefore, the measurements provide a basis for evaluating the hazard under normal conditions. Based on the low contribution to LFL, this hazard poses no significant risk under normal conditions for any of the operations described in Table 7-1.

Process upsets associated with the operations described in Table 7-1 do not have a credible potential for significantly increasing NPH-TBP vapors in headspace air. This is so because the pool would have to be heated to $-72\text{ }^{\circ}\text{C}$ for vapors to contribute 25% of the LFL. Based on interpolation of the concentration versus temperature data of Table 5-3, 25% of the LFL ($0.25 \times 47\text{ mg/L}$) would be attained at equilibrium at a temperature of $-72\text{ }^{\circ}\text{C}$. None of the operations, under upset conditions, can cause the heating of the liquid from its present temperature ($-40\text{ }^{\circ}\text{C}$) to $72\text{ }^{\circ}\text{C}$. An additional mitigating factor is that the measured flashpoint of the organic liquid ($118 \pm 2\text{ }^{\circ}\text{C}$) is higher than the temperature where water vapor would inert the headspace ($-72\text{ }^{\circ}\text{C}$, see Section 6.2.2.1). Based on the discussion above, this hazard does not pose a credible risk under operation upset conditions for any of the operations described in Table 7-1.

7.2.1.2 Organic Layer Aerosol Generation. Both visual observations and theoretical analyses (Sections 5.6 and 6.1.3) indicate that airborne concentrations of organic aerosols represent less than 1% of the LFL. None of the operations described in Table 7-1 appear to have the potential to cause the formation of organic aerosol, and hence this hazard poses no significant risk under normal operating conditions.

Enhanced aerosol formation would require either a substantial global heating of the organic layer or the input of mechanical energy that was effective in atomizing the organic liquid. None of the operations described in Table 7-1, under upset conditions, causes either of the two changes required for enhanced aerosol formation; hence, this hazard poses no credible risk under operational upset conditions.

7.2.1.3 Combustible Species Produced by Radiolytic and Other Chemical Reactions. Tank C-103 has a relatively high decay heat load, and therefore may be expected to produce radiolytic species such as hydrogen at a higher rate than tanks with lower decay heat loads. As discussed in Section 6.1.2, airborne radiolytic species build in concentration to an equilibrium level where the production rate is equal to the removal rate by ventilation. Higher equilibrium concentrations correspond to lower ventilation rates. In addition, the vent path, (i.e., venting via cascade lines through tank C-102 or C-101) can also affect the equilibrium airborne concentration.

Ventilation flowrate is the sum of flows arising from the following:

- Atmospheric pressure fluctuations
- Air purge into level measuring gauges
- Leakage induced by natural convection
- Operation of a portable exhauster.

A portable exhauster, if used, would induce flow rates that would dominate compared to the other three causes described above and would cause a significant decrease in equilibrium airborne concentrations of radiolytic species. Therefore, it is clear that operation of an exhauster would not pose a risk in relation to radiolytic species buildup.

The one operation listed in Table 7-1 that could affect ventilation flow rate is entitled "Passive Tank Ventilation."

The concentration of radiolytic species could increase from present levels if one or more of the following changes were to take place:

- Reduction in air purge flow rate
- Closing vent valve on tank C-102 without opening vent valve on C-103
- Change valving to cause tanks C-103, -102, and -101 to vent through tank C-101
- Additional sealing of pit covers and other leaks that bypass filtered vents.

The predicted increase in the concentration of radiolytic species following the assumed termination of purge air in both tanks C-102 and C-103, amounts to a factor of 5.6 compared to current equilibrium levels (Table 6-2). The increase in concentration of combustible species can be estimated by multiplying the present concentration of radiolytic species by 5.6, and then adding the concentration of NPH-TBP components that are in equilibrium with the pool. Hydrogen, carbon monoxide, methane, and ammonia currently sum to a total of $2.3 \pm 0.1\%$ of the LFL (Section 5.6.1). An estimate of radiolytic organic species may be obtained by subtracting from total non-methane organics ($2.3 \pm 0.4 \text{ g/m}^3$) the NPH component concentration deduced from headspace air samples ($1.2 \pm 0.25 \text{ g/m}^3$). The difference, $1.1 \pm 0.65 \text{ g/m}^3$ represents an estimated of radiolytic organic species. Using an estimated LFL of 47 g/m^3 for radiolytic organics, the radiolytic organic species are calculated to amount to $2.3 \pm 1.4\%$ of LFL. An estimate of the current total radiolytic species, organics plus inorganics, amounts to $4.6 \pm 1.5\%$ of the LFL. When this value is increased by a factor of 5.6 and added to NPH-derived species, the result is $27 \pm 8.7\%$ of the LFL. This value is marginally higher than the target maximum of 25% LFL, and suggests that the total termination of purge-air flow could lead to combustible species concentrations that exceeded the 25% LFL criterion.

The worst-case upset condition for passive tank ventilation is the hypothetical case in which air purge is terminated, all three vent valves are closed, and bypass leakage is zero. This case is worth considering because it can be shown that the response time is relatively long, allowing ample time for detection and correction. A transient analysis was done for the assumed total stoppage of ventilation in all three tanks (C-101, C-102, and C-103). A radiolytic source term, proportional to estimated decay heat load was assigned to each tank as described in Section 6.1.2.1. Radiolytic concentrations are calculated to increase linearly with time. The time required to double the current concentration is ~ 70 days. The calculated time to reach 25% LFL (based on a current radiolytic species concentration of 4.6% LFL) is 270 days.

A final case analyzed here involves the venting of each tank to the atmosphere through its own vent valve. If purge air in tank C-103 were terminated and simultaneously the vent valve were opened so that tank C-103 breathed directly to the atmosphere, the concentration of radiolytic gases is calculated to increase by a factor of $(1.4 \pm 0.48)/(0.48)$ (1.24) or 3.2. This factor is based on the ratio of ventilation flow rates and a pathway factor (1.24) as discussed in Section 6.1.2.1. Total combustibles are predicted to peak out at $(4.6 \pm 1.5\% \text{ LFL}) (3.2) + 2.5 \pm 0.5\% \text{ LFL}$ or $17.2 \pm 5.3\% \text{ LFL}$. This calculated peak value falls below the 25% LFL criterion, indicating that the deflagration hazard can be controlled by simply venting tank C-103 directly to the atmosphere.

In summary, changes in purge-air flow rate and vent valve settings could cause combustible species to increase in concentration to greater than the 25% LFL criterion. In all cases the buildup rate is predicted to slow; a worst-case (zero ventilation) calculation showed that the 25% LFL criterion would be reached in 270 days. On a more realistic note, the analysis showed that peak concentrations remained below the 25% LFL if each tank was vented directly to the atmosphere, even if purge air were zero.

The following controls on ventilation appear to be adequate to maintain headspace combustibles below the 25% LFL.

1. Semiannual monitoring of headspace air to confirm that changes in purge rates, vent valve settings, or reductions in naturally convected air flows have not reduced ventilation to a level where combustibles exceed the 25% LFL criterion.
2. As an alternative to (1) above, a control that requires each tank (C-103, C-102, and C-101) to be vented directly to the atmosphere along with annual monitoring of combustible levels appears to be sufficient to ensure that the 25% LFL criterion would not be exceeded. While the analysis described earlier in this section indicates that combustibles could not reach the 25% LFL level, if tank C-103 were vented to the atmosphere, annual monitoring would provide a backup check of the calculations would identify a situation where operational errors in vent valve settings had been made, and would identify the unlikely event of vent path plugging.

7.2.2 Summary of Pool Fire Hazard

The safety basis for a pool fire in tank C-103 is the prevention of ignition of such a fire. As discussed in Section 6.2, the ignition of a pool fire for liquids subcooled with respect to the fire point requires the introduction of energy to heat the liquid, and an igniter in the vicinity of the air/liquid interface. An energy input of approximately 1.2 MJ is estimated as a minimum requirement on the basis of tests (Malet et al. 1983) with fresh NPH-TBP solutions. Because the organic in tank C-103 has been stripped of the most volatile

components, it has a higher flashpoint than fresh materials and would have to be heated to higher temperatures than the fresh material tested by Malet (1983). Therefore energy required to initiate a pool fire in tank C-103 is probably greater than the 1.2 MJ cited above.

Under normal conditions, none of the operations described in Table 7-1 have the potential to ignite a pool fire, and therefore pose no risk in terms of this hazard.

Under upset (accident) conditions, each operation needs to be examined for the potential of introducing an energy of ~1.2 MJ into the organic liquid. An operation-by-operation discussion is provided in the following section.

To ensure that the pool is not ignited, controls and monitoring that address ignition are appropriate. These include the following tasks:

1. Prevent the introduction of energetic ignition sources
2. Prevent the introduction of wicks
3. Monitor waste level to verify that the pool continues to float on aqueous supernatant liquid.

7.2.3 Summary of Organic-Nitrate/Nitrite Reaction Hazard in Organic Liquid

The hazard of uncontrolled exothermic reactions in the organic liquid has been investigated by adiabatic calorimetry tests carried out under an overpressure of 400 lb/in² gauge (see Section 5.1.4). The absence of significant exothermic activity over a temperature range from room temperature to 440 °C is evidence that this hazard poses no risk. No controls or monitoring are needed for this hazard.

7.2.4 Summary of Organic-Nitrate/Nitrite Reactions in Sludge

Two properties of the sludge provide assurance that this hazard poses no significant risk:

1. The sludge is wet, being submerged beneath aqueous supernatant liquid
2. Organic carbon levels in sludge are too low to sustain a propagating reaction even under a hypothetical dry condition.

No controls or monitoring are needed for this hazard.

7.3 HAZARDS ASSESSMENT FOR SPECIFIC OPERATIONS

In this section, each of the operations listed in Table 7-1 is described in terms of normal and upset conditions. The focus is on upset conditions and on how such conditions could exacerbate the pool fire hazard. As described in Section 7.1, most other hazards do not pose risks in relation to identified operation. The one exception is "passive ventilation" which is important in relation to headspace deflagrations. This one deflagration/operation pair was discussed in detail in Section 7.2.1.3 and will not be included here.

7.3.1 Liquid Level Monitoring

Three direct methods for determining the liquid level of the single-shell tanks are currently in use: FIC gauge, manual tape, and zip cord.

FIC GAGE

The associated equipment for the FIC systems consists of a plummet suspended on a steel tape, tape reel, sight glass, control switch, and ports for air purge and water flush. The FIC gauges are mounted on designated tank risers. The control systems automatically adjust the tape position so that the plummet repeatedly makes and breaks contact with the waste surface. The completion of the electrical circuit through the plummet gives the reading. The FIC gauge uses a 110 VAC source which is stepped down by a transformer to 24 VAC. There is a current limiting resistor of 100,000 ohms in series with the plummet.

MANUAL TAPE AND ZIP CORDS

The manual tape system consists of either reel-mounted tapes, or calibrated insulated wire to which an electrode has been attached. The reel and spool assembly are permanently attached to the tank riser flanges, and the insulated wires (Zip Cords) are inserted beneath the riser flange cover plate. Readings are obtained by the continuous reading of a portable DC meter or by feeling the plummet touch the surface.

A zip cord is an insulated wire to which electrodes have been attached and is pre-measured and marked. It is similar to the manual tape with the exception that it is not permanently attached. The zip cord is lowered through a riser. Continuity across the electrodes, shown with a portable DC meter, indicates contact with the liquid level and the length of cord is read from the pre-measured markings on the cord. Typical equipment uses 1.5 volt and less than 0.35 milliamp source for determining continuity.

UPSET CONDITIONS

Shorting out of the FIC's step-down transformer could apply 110 VAC (through the current-limiting resistor) to the plummet in contact with the organic liquid during level measurements. Analysis of this fault condition (Scaief 1991) showed the spark energy to be too small to ignite a hydrogen-air mixture. Because a pool fire requires energy additions, many orders of magnitude higher than ignition of a flammable H₂-air mixture, the level measuring devices do not pose a threat for pool fires.

7.3.2 Sludge-Level Monitoring

Sludge-level readings use a simple steel doughnut. This is attached to the bottom of a calibrated tape or wire and is lowered into the tank. When it comes to rest in the sludge, the tape or wire slackens. A reading is then taken from the reference point, such as the top of the riser.

UPSET CONDITIONS

The steel doughnut and support tape could be dropped into the tank. Falling objects cannot heat the organic to the flashpoint, and hence this operation poses no threat for pool fires.

7.3.3 Temperature Monitoring

Temperature monitoring uses a thermoelectric device called a thermocouple. More than one thermocouple, for readings at varying depths, on a device is referred to as a thermocouple tree (TCT).

Typically, a TCT is 3 in. in diameter and 20 to 30 ft in length. All of the thermocouples are isolated and sealed inside the steel TCT in what is called a thermowell.

ACCIDENT CONDITIONS

A lightning strike during installation/removal is the only initiator capable of introducing a significant amount of energy to the organic layer. Storm warning procedures (TO-020-270) and the probability of a lightning strike during installation make the overall probability of occurrence $4.2E-9$ (Farley 1992).

In addition to the low probability of a lightning strike, the operation envisioned here deals only with a thermocouple tree that has a replaceable core. Therefore, the lightning arc

would probably be localized at a site other than the organic-air interface. It is concluded that the probability of this accident condition is too low to be considered a credible initiator for a pool fire.

7.3.4 Still Camera Photography

The system to be used is a standard 70 mm still camera and flash unit mounted in a metal frame. The system is suspended in the tank by a flexible support hose containing wiring going to the camera and flash unit. Power to the flash unit is supplied by a portable generator on the ground surface above the tank. The wiring is sealed but not intrinsically safe. The camera and flash unit are manually lowered into the tank to a level controlled by an adjustable safety stop (top hat) at the top of the riser. Contamination control to the camera system is implemented by lining the riser with a disposable plastic sleeve.

UPSET CONDITIONS

- If the camera was dropped and the safety "top hat" failed, there would be no electrical sparking at the waste surface, because for the camera to fall to the waste surface, the electrical cable would have to break, and this would disconnect the camera and flash from the surface located electrical power supply.
- The failure of a flash unit, allowing the hot filament to fall to the waste surface, allows a small amount of energy to be applied to the organic layer (Van Vleet [1991] estimates 67 J available from a filament cooling down from 2000 °C to 180 °C).
- If a "top hat" was not used, the flash unit could be lowered into the organic layer. Shorting of connections within the organic liquid could conceivably dissipate energy from the 110 VAC supply line and heat the organic locally.

The energy from the first two of these upsets is too small to initiate a pool fire. The energy from the first two upset conditions is too small to initiate a pool fire. The third upset can be dealt with by imposing an operational control that prevents the use of power supply cords long enough to reach the organic-air interface (see Section 8.2).

7.3.5 Video Camera Operations

The video equipment will consist of a standard video camera with pan and tilt capabilities along with illumination lights. The entire unit is connected to a support stem. The camera system is supported to a shield plug which limits the length the camera system can intrude into the tank and maintains tank integrity.

UPSET CONDITIONS

- If the camera support stem failed, there would be no electrical sparking at the waste surface, because for the camera to fall to the waste surface, the electrical cable would have to break, and this would disconnect the camera, pan and tilt, and light from the surface located electrical power supply.
- The failure of a light unit, allowing the hot filament to fall to the waste surface, allows a small amount of energy to be applied to the organic layer (Van Vleet [1991] estimates 67 J available from a filament cooling down from 2000 °C to 180 °C).
- If a "top hat" was not used, the flash unit could be lowered into the organic layer. Shorting of connections within the organic liquid could conceivably dissipate energy from the 110 VAC supply line and heat the organic locally.

The energy from the first two upset conditions is too small to initiate a pool fire. The third upset can be dealt with by imposing an operational control that prevents the use of power supply cords long enough to reach the organic-air interface (see Section 8.2).

7.3.6 Portable Exhauster Operations

The portable exhauster (nominal 1000 CFM) is mounted on a mobile platform and is positioned above the tank. The portable exhauster uses a 12 in. flexible duct bolted to a tank riser.

Most portable exhausters have the following equipment, in order of air flow:

- A deentrainer to remove large moisture particles
- A plenum to direct and control airflow
- A preheater to lower relative humidity in the airstream
- A roughing filter to screen large particles ahead of the HEPA Filters
- Two banks of HEPA Filters in series
- A manual damper to regulate airflow
- A fan/blower(s) to pull air through the system
- A stack to direct exhaust air
- An air sampler to collect record sample of radioactive particles
- A continuous air monitor which detects radioactive particulates in the exhaust
- A seal pot to collect moisture from the system.

UPSET CONDITIONS

Failure of the exhauster could cause sparks and hot components, e.g., bearings. However these would be exterior to the tank and hence could not initiate a pool fire.

7.3.7 Pit Cover Block

The cover block is a concrete slab used primarily for radiation shielding and protection of the pump or valve pits. Because of their size and weight, these are only removed and installed with a crane operation using the embedded lifting rings of the cover block.

A cover plate is usually a one-quarter-inch thick steel plate. In waste tanks where there is a lower source term, cover plates may be used as a substitute for the cover block to provide protection to a pit.

UPSET CONDITIONS

Accidental dropping of a cover block into the pit could cause local sparking and structural damage to equipment in the pit. Such effect would be exterior to the tank and could not initiate a pool fire. Likewise, dropping of a cover block onto a riser or TCT might result in fractured material entering the tank. Such materials would be low in temperature and could not initiate a pool fire.

7.3.8 Riser Flange and Gasket

Numerous vertical pipes (risers) penetrate the tank dome at difficult depths of the tank. Common diameters of the risers are 4 in., 12 in., and 42 in.

Gaskets are used to ensure tank integrity at the riser/flange interface. Older gaskets are asbestos and need to be handled with care.

UPSET CONDITIONS

Removal/replacement of flanges and gaskets could result in dropping accidents, generating local sparks, and the dropping of gasket pieces into the tank. While neither of these conditions could initiate a pool fire, the dropping of gasket materials into the tank needs to be avoided because such materials could conceivably act as wicks. Wick-like materials are prohibited from use inside of the tank (Section 8.2).

7.3.9 Riser Modifications

Material additions (such as spools) to raise or lower the flange to accommodate various equipment are considered riser modifications. Installing plugs or blanks on the riser with the removal of existing equipment is another type of riser modification considered.

Riser modifications as defined here, do not include physical (permanent) modification to the riser itself, such as cutting or welding operations. It only refers to a change in its configuration.

UPSET CONDITIONS

Upset conditions are similar to those described in Section 7.3.8, and similar comments apply.

7.3.10 Waste Sampling - Vapor Space

The typical equipment for vapor space sampling is made up of the gas-sampling probe assembly and the various sampling equipment.

A typical sample probe has three main components:

1. Sample tubes: 0.22 or 0.5 in. inner diameter Teflon* or Teflon-equivalent tubing with helical wound stainless steel wire.
2. Sampling riser cover: a one-quarter-inch thick, carbon steel plate with drilled holes to match the riser flange bolt pattern and holes for the sample ports.
3. Sample ports: Stainless steel tubes protruding through the sampling riser cover. The bottom side is connected to the sampling tubes. The top side is connected to shutoff valves and the various sampling equipment.

The sampling equipment usually includes a combustible gas meter, an organic vapor monitor, and a hydrogen sampling cart assembly. These are attached to the sampling ports once the sampling riser has replaced the existing riser cover. Samples are obtained by following standard tank farm operating procedures for the equipment.

The area around the tank breather filter is sampled for flammable and toxic gases at the beginning of the task. The riser is also sampled for flammable gas when the riser cover is first removed.

*Teflon is a trademark of E. I. Dupont Co., Wilmington, DE.

UPSET CONDITIONS

No upset conditions that could affect the pool-air interface have been identified.

7.3.11 Waste Sampling - Liquid

Liquid sampling is a standard tank farm procedure covered by WHC document TO-080-030. A 100 ml glass sampling bottle with a rubber stopper is placed in a 2 in. steel pipe sleeve and manually lowered on a stainless steel wire to the supernate waste. The weight of the pipe sleeve submerges the bottle. The wire is looped through the top of the rubber stopper and tied to the neck of the bottle. After lowering the bottle to the proper level, a quick jerk removes the rubber stopper and the bottle fills with liquid. After a bottle is filled, the bottle is manually pulled to the surface by a worker wearing protective gloves.

A Health Physics technician (HPT) monitors the sample line and sample bottle for radiation as it is retrieved. Before removing the bottle from the top of the riser, the bottle is sealed with a screw on cap. The sample bottle is lowered one foot into the riser and washed down with warm water. After shaking off the excess surface water, the sample bottle is removed from the riser, checked by the HPT, placed in a plastic bag, and then placed in a protective container (sample pig). After the pig is checked for radiation by the HPT, the pig is placed in a shipping container for transport of the sample to an analytical laboratory.

UPSET CONDITIONS

Because this operation involves removal of a riser cover, accidents involving dropped objects could occur. Dropped objects of ambient temperature cannot initiate a pool fire.

7.3.12 Waste Sampling - Push-Mode Core

The core sample truck has a rotary platform mounted on the rear of the truck. Two sets of equipment are mounted on the rotary platform. One set is the shielded sample receiver unit that functions to place empty samplers into and remove full samplers from the drill string. The other set of equipment is the drill unit that functions to push the drill string and sampler into the material being sampled. A control console and electric hoist are also mounted on the rotary platform. The following paragraphs briefly summarize the sampling procedure.

The core drill truck is positioned over the riser of interest. The truck is leveled and the riser adapter, spray washer assembly, and pneumatic foot clamp is installed. The pneumatic foot clamp provides one of the physical restraints to prevent the drill string from being dropped into the tank during installation and removal of the drill string.

To perform the sampling, the first core sampler is inserted into the drill string core barrel. The drill string is attached to the core barrel and then extended a section at a time. The drill string is lowered into the tank using the hoist, the pneumatic foot clamp is activated to physically restrain the drill string, and the hoist is disengaged. Then a new section of drill string is threaded onto the existing drill string, the hoist is reattached (providing a physical restraint to dropping the drill string), and the foot clamp is disengaged. This continues until the sampler is just above the surface of the waste. The drill unit is attached to the drill string. The drill unit then pushes the drill string 48 cm (19 in.) into the waste. A rotary valve is closed at the bottom of the sampler, hydrostatic fluid is added inside the drill string, and the drill string is detached from the drill unit.

The platform is rotated so that the shielded receiver is over the drill string. The sampler is raised into the shielded receiver. A ball valve is closed at the bottom of the shielded receiver. A kamlock cap with an absorbent sponge is attached to the bottom of the shielded receiver. The platform is rotated to position the shielded receiver over the empty transfer cask. The kamlock cap is removed and the sampler is lowered into the transfer cask. A new sampler is placed in the core barrel. The total process is repeated until a full core sample is achieved.

UPSET/ACCIDENT CONDITIONS

- Gasoline spill from sampling truck which leaks into the 241-C-103 and is ignited.
- Lightning strike during operation, removal and installation of the push-mode sampling truck. Storm warning procedures (TO-020-270) and the probability of a lightning strike during installation make the overall probability of occurrence $4.2E-9$ (Farley 1992).

Both of these accidents have potential for initiating a pool fire. The probability of a lightning strike is known to be low, as referenced above.

The fuel spill accident has been analyzed (see Appendix E) and could not be ruled out as a credible event. Mitigating controls have been initiated to reduce the probability of occurrence by two orders of magnitude (Section 8.3). Ensuring that vehicles entering the area use propane, have fuel tank skid plates, or are high enough off of the ground to prevent contact with the tank risers reduces the probability of occurrence to less than 1×10^{-6} events/year.

7.3.13 Addition of High-Level Waste

The several pits and associated piping were designed to allow the transfer of waste to and from the tank. The destination is determined by the arrangement of jumpers (flexible piping)

between the existing underground lines. Normally, when transfers have been completed or lines are inactive, the ends are capped off, isolating the lines.

Transferring of waste is only made during the interim stabilization of the single-shell tanks. When a transfer occurs, waste is moved from a single-shell tank and into a double-shell tank. The transfer of waste into a single shell tank is prohibited with administrative controls in place to preclude this from occurring.

Before making a transfer of waste, it is required to pressure test the lines that will be used to make the transfer. Tanks where waste is not to be transferred into are blank off (isolated) using standard tank farm procedures. The lines are pressurized and need to maintain pressure for a given period of time. The configuration of the transfers lines remains unchanged until after the transfer is completed.

UPSET CONDITIONS

While no specific upset conditions have been identified, the addition of flammable, low flashpoint organic liquids should be prevented. Such wastes could make the pool easier to ignite, and should be precluded by imposed controls.

7.3.14 Small Volume Water Additions

Small volumes of water may be introduced into the tank for various flushing operations (dip tube, pump, pit). Water is also used to decontaminate operations such as liquid sampling.

The water amount is strictly controlled and monitored through standard tank farm procedures.

UPSET CONDITIONS

No upset conditions related to pool fire initiation have been identified.

7.3.15 Breather/Sorbent Beds

High efficiency particulate air (HEPA) breather filters have been installed on all single-shell underground waste storage tanks. The HEPA serves to filter out radioactive particles. Two Sorbent beds have been installed on tank C-103 downstream of the HEPA filter. One of these filters serves to organic vapors and the other one traps ammonia.

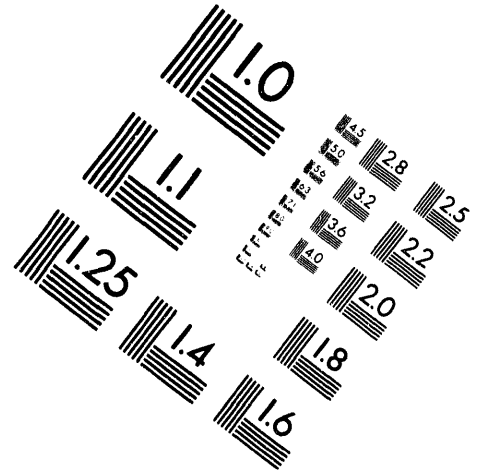
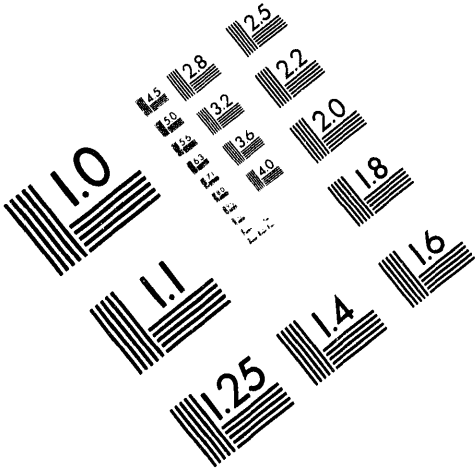
Isolation valves are installed between the filter and the tank to maintain integrity of the tank during maintenance of these filters.



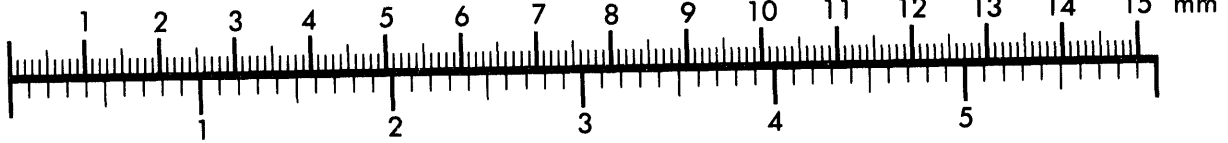
AIM

Association for Information and Image Management

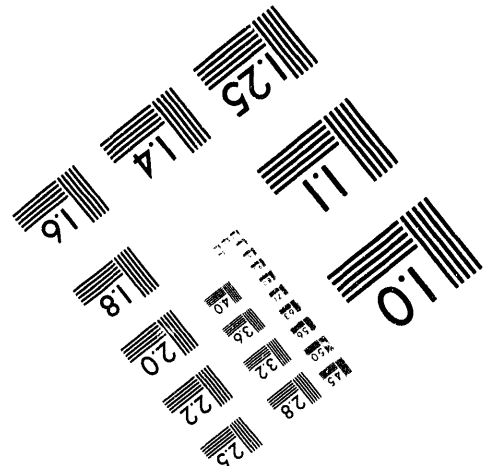
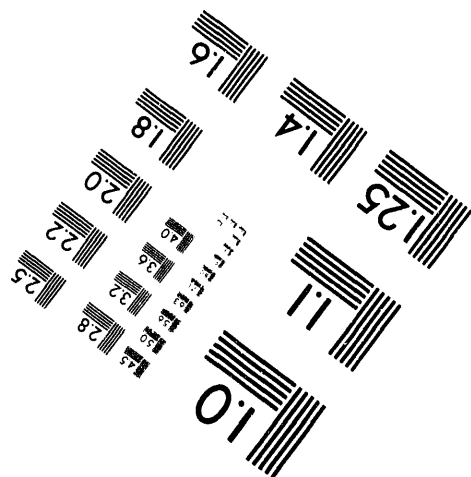
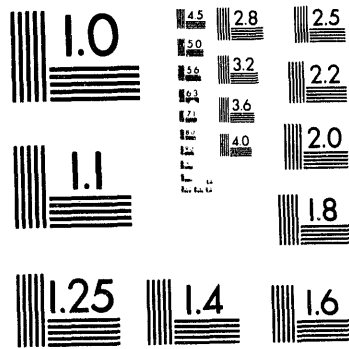
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202



Centimeter



Inches



MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

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UPSET CONDITIONS

Plugging of this filter train could impair ventilation caused by atmospheric pressure variations, if purge air were terminated. Any reduction in ventilation flow could impact deflagration hazard as discussed in Section 7.2.1.3. A monitoring requirement for combustible gases (see Section 8.1) limits combustibles to 25% of the LFL and thereby prevents filter train plugging from becoming an accident initiator.

No upset conditions related to pool fire initiation have been identified.

**8.0 CONTROLS AND MONITORING REQUIRED
FOR SAFE INTERIM STORAGE**

On the basis of the hazards assessments described in Section 7.0, the following controls and monitoring requirements are prescribed. Equivalent controls and monitoring to preclude headspace deflagration or pool fires that meet or exceed those described below are acceptable.

**8.1 CONTROLS AND MONITORING RELATED TO
HEADSPACE DEFLAGRATIONS**

The safety basis for this hazard is to maintain combustible species concentrations (the total of all species) below the LFL. This will preclude the occurrence of a headspace deflagration. To provide a margin of safety, the maximum acceptable concentration of combustible species is specified as 25% of the LFL in conformance with NFPA 497A (NFPA 1986). Available information on how combustible species may be generated and removed from headspace air indicates that the 25% LFL target can be met by imposing minimal controls, and therefore that headspace deflagrations can be precluded.

As discussed in Section 7.2.1, the organic liquid can add significantly to headspace combustibles only if the liquid is heated significantly above current temperatures. None of the operations described in Section 7.0 can significantly heat the organic liquid. Therefore, no controls are needed to prevent the organic liquid from becoming a credible deflagration hazard.

The equilibrium concentration of combustible species produced by radiolysis and other first order reaction kinetics is directly related to the headspace ventilation rate. Controls and monitoring are needed to make sure that ventilation is sufficient to prevent the buildup of radiolytic species to higher than 25% of the LFL.

Either of the following operational controls and monitoring requirements is deemed to be sufficient to preclude a headspace deflagration during interim storage.

1. The headspace air in tank C-103 shall be monitored on a semiannual cycle to verify that combustible concentrations are at or below 25% of the LFL, or
2. Tank C-103 shall be vented directly to the atmosphere through its own breather vent and combustible concentrations shall be monitored on an annual cycle to verify that combustibles remain at or below 25% of the LFL.

8.2 CONTROLS AND MONITORING RELATED TO POOL FIRE INITIATION

The safety basis for potential pool fires in tank C-103 is to prevent their initiation. This approach is technically feasible because a pool fire in this tank would, at present, be difficult to initiate. The following controls and monitoring requirements are deemed sufficient to prevent the initiation of a pool fire in tank C-103 during interim storage.

1. Fire, flaming objects, or hot materials ($T > 120\text{ }^{\circ}\text{C}$) shall not be permitted in the vicinity of an open riser. In the vicinity means that there is a credible chance that the prohibited material could enter the tank through an open riser. The objective of this control is to preclude the introduction of igniters at the pool-air interface. The prohibited materials do not include small filaments included in lighting or electronic equipment because such filaments are both small and enclosed within solid boundaries.
2. Electrical equipment used in tank C-103, such as flood lights and cameras, shall be suspended by electrical supply cords whose length is too small to permit the equipment or its supply cord from approaching within 5 ft of the pool surface. This control is imposed to avoid the possibility of electric power dissipation in the vicinity of the organic liquid-air interface.
3. Porous materials which could serve as wicks for a wick-stabilized flame shall be prevented from entering the tank. The objective of this control is to minimize the presence of wicks at the organic-air interface. As described in Section 6.0, a wick-stabilized flame is easier to ignite than a fire on an open pool. This prohibition does not apply to equipment or processes that may be used to remove the organic liquid from tank C-103. The risk posed by wick-stabilized fires would have to be evaluated for any removal process that employed porous wick-like materials.
4. Waste surface level (organic or aqueous) shall be monitored. As noted in Section 7.0, one of the factors that makes the pool difficult to ignite is that it floats on several feet of water. If the water were to leak, allowing the organic to float directly on sludge, pool fire initiation would have to be re-evaluated.

5. Vehicles operating at grade level over tank C-103 must employ fuels or fuel tank protection that greatly reduces the chance for an accident in which ignitable liquid fuel could enter tank C-103. Controls that have been evaluated as acceptable include any of the following.
- The vehicle must be propane fueled.
 - The vehicle must have a protective plate (skid plate) protecting the fuel tank and any reservoir tanks from contacting risers protruding above grade.
 - The fuel tank (and any reservoir tank) must be physically located at a height greater than the highest riser that would impact a tank located at a lower level.

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APPENDIX A
TANK 241-C-103 ORGANIC LAYER FLASHPOINT

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APPENDIX A

TANK 241-C-103 ORGANIC LAYER FLASHPOINT

A.1 INTRODUCTION

An important parameter describing the flammability of the organic layer in tank 241-C-103 is its flashpoint. The flashpoint is the temperature at which vapors (in equilibrium) above the layer attain incipient flammability. In practice, this means that a pressure rise indicating non-negligible combustion is observed when an ignition source is applied above a heated liquid sample. The vapor composition at incipient flammability is defined as the lower flammability limit (LFL) and the flashpoint is thereby a point on the vapor pressure curve of the substance. Indeed, since the LFL is observed to decrease with increasing temperature at constant pressure (here assumed to be 1 atm), the flashpoint is the intersection of the LFL concentration curve as a function of temperature and the vapor concentration curve.

Experimental determination of the flashpoint is difficult for mixtures similar to the C-103 organic layer for reasons like the presence of compounds with widely varying vapor pressure and flammability characteristics which will be discussed below. However, the definitions above allow theoretical prediction of the flashpoint. This appendix will present existing flashpoint data for TBP and NPH, and provide analytical predictions for their mixtures and the C-103 layer.

A.2 FLASHPOINT DATA OF PURE COMPOUNDS

The flashpoints and LFLs of NPH compounds formerly and presently comprising the C-103 organic layer are correlated by the U.S. Bureau of Mines (Kuchta 1985) by means of the following two equations:

$$T_f(n) = \sqrt{10410n} - 2773 \quad (\text{A-1})$$

$$\frac{1}{L(n)} = \frac{10410n + 3365}{77291} \quad (A-2)$$

where:

- n = Carbon number (10 = decane, 11 = undecane, etc.)
- T_f(n) = Flashpoint, °C
- L(n) = LFL, volume %, at T_f(n).

Since the LFL will decrease nearly linearly to zero at about 1300 °C, the LFL may be conservatively modified for this effect by the following equation:

$$L(T,n) = L(n) \left[1 - \frac{\max(0, T - T_f(n))}{1300 - T_f(n)} \right] \quad (A-3)$$

where:

- T = Temperature, °C, and
- max(a,b) = Maximum of the two arguments.

In practice, the denominator of the modifying fraction may be simplified to 1000. The flashpoints and LFL is calculated by means of Equation (A-1) and Equation (A-2) respectively for n = 10 to 14 are listed in Table A-1.

Table A-1. Flashpoint and LFL of Selected NPHs.

Compound	Carbon number (n)	Flashpoint (T _f , °C)	LFL (volume %)
Decane	10	47.7	0.719
Undecane	11	63.2	0.656
Dodecane	12	77.5	0.602
Tridecane	13	92.5	0.557
Tetradecane	14	103.8	0.518

Vapor pressures for these NPH compounds may be estimated from the three-parameter Antoine equation:

$$\log_{10}P = A - B/(T+C) - \log_{10}760 \quad (\text{A-4})$$

where:

P = Pressure, atm

T = Temperature, °C

and A, B, and C are constants for each NPH listed in Table A-2.

Table A-2. Vapor Pressure Correlations for NPH and TBP.

Component	A*	B*	C*
Decane, C ₁₀ H ₂₂	6.94365	1495.17	193.86
Undecane, C ₁₁ H ₂₄	6.97220	1569.57	187.70
Dodecane, C ₁₂ H ₂₆	6.99795	1639.27	181.84
Tridecane, C ₁₃ H ₂₈	7.00756	1690.67	174.22
Tetradecane, C ₁₄ H ₃₀	7.013	1740.88	167.72
TBP, (C ₄ H ₉ O) ₃ PO	8.527	3173.0	273.16

*NPH vapor pressure constants from Dean (1985)

The TBP vapor pressure curve may be estimated using the reported values of 289 °C for its normal boiling point and a vapor pressure of 0.1 mmHg at 60 °C (Gerber 1992), yielding Antoine constants in Table A-2. Using this vapor pressure correlation, the LFL for TBP is 4.57% at the measured flashpoint of 181 °C (Pool and Bean 1994).

For reference, volume concentrations of the NPH compounds and TBP near 100 °C are listed in Table A-3. Note that these compounds almost follow the rule of thumb that vapor pressures double with a 10 °C temperature rise (i.e., a factor of 8 in pressure is manifest over a 40 °C temperature range).

Table A-3. Calculated Vapor Concentrations for NPH and TBP at 80 °C, 100 °C, and 120 °C.

Compound	Vapor concentration, volume %		
	80 °C	100 °C	120 °C
Decane	4.0	9.4	20.
Undecane	1.7	4.3	9.8
Dodecane	0.72	2.0	4.9
Tridecane	0.30	0.92	2.4
Tetradecane	0.13	0.43	1.2
TBP	0.046	0.14	0.38

A.3 FLASHPOINT CALCULATION FOR NPH-TBP MIXTURES

Using LeChatelier's law (Kuchta 1985) for the LFL of a vapor mixture the flashpoint of an NPH-TBP mixture is given implicitly by

$$1 = \sum_{i=1}^6 \frac{\gamma_i X_i P_i(T_f)}{L_i(T_f)} \quad (\text{A-5})$$

where:

- T_f = Flashpoint, °C
- γ_i = Activity coefficient
- X_i = Mole fraction
- P_i = Vapor pressure, atm
- L_i = LFL, volume fraction

and $i = 1$ to 5 are the NPH components mentioned above and $i = 6$ is TBP. Note that with a total pressure of $P = 1$ atm, and P_i also in atm, P_i are numerically equal to concentration in mole (volume) fraction.

A.4 IDEAL FLASHPOINTS FOR THE C-103 LIQUID SAMPLE

Table A-4 recasts the relative weight fractions and mole fractions found in the C-103 liquid sample listed in Table 5-1 of the main body of this report using a combining method as follows.

Table A-4. C-103 Sample Analysis, Adjusted Fractions.

Compound	Weight percent	Mole percent
TBP	66.6	58.3
Dodecane	5.6	7.7
Tridecane	17.4	22.0
Tetradecane	10.3	12.1

Volatile alkanes found between major NPHs were lumped with the next most volatile NPH, and dibutyl butyl phosphonate (DBBP) was lumped with TBP.

The ideal flashpoint of this composition is 106 °C (223 °F). Note that the flashpoint is controlled by the NPH components. For example, artificially employing 150 °C (°F) for the TBP flashpoint (versus 181 °C) yields a mixture flashpoint of 105 °C, (°F) only 1 °C (°F) lower.

A greater impact is made by the use of the relative mole fraction. If mole percents of Table A-4 are multiplied by 0.74 to account for the involatiles in the sample, then the ideal flashpoint of the mixture is 111 °C using a TBP flashpoint of 150 °C (°F).

The impact of conservative combining may be checked by instead combining unidentified alkanes with less volatile NPH. The weight percents for the NPH compounds of Table A-4 become 3.8, 17.3, and 12.2 (starting with dodecane) under this scheme. Also invoking the factor of 0.74 to account for involatiles, and using 181 °C (°F) for the TBP flashpoint, the C-103 organic layer flashpoint is 114 °C (237 °F).

In conclusion, the ideal organic layer flashpoint is calculated in the range of 105 °C (221 °F) to 114 °C (237 °F).

A.5 NON-IDEAL FLASHPOINT FOR THE C-103 LIQUID SAMPLE

Vapor concentrations measured above heated C-103 organic liquid samples (Pool and Bean 1994) may be compared with the correlations used above to yield effective activity coefficients for each compound. The activity coefficient of a compound is the ratio of observed to ideal vapor concentration using the mole fractions assumed in Table A-4 above:

$$\gamma_i = \frac{P_{i,data} R (T+273)}{X_i P_i (T) MW_i 10^5} \quad (A-6)$$

where:

- $P_{i,data}$ = Concentration, mg/L, observed
- R = 3.314, ideal gas constant
- T = Temperature, °C
- MW_i = Molecular weight
- 10^5 = Conversion of atm to Pa

The observed data and derived activities are listed in Table A-5.

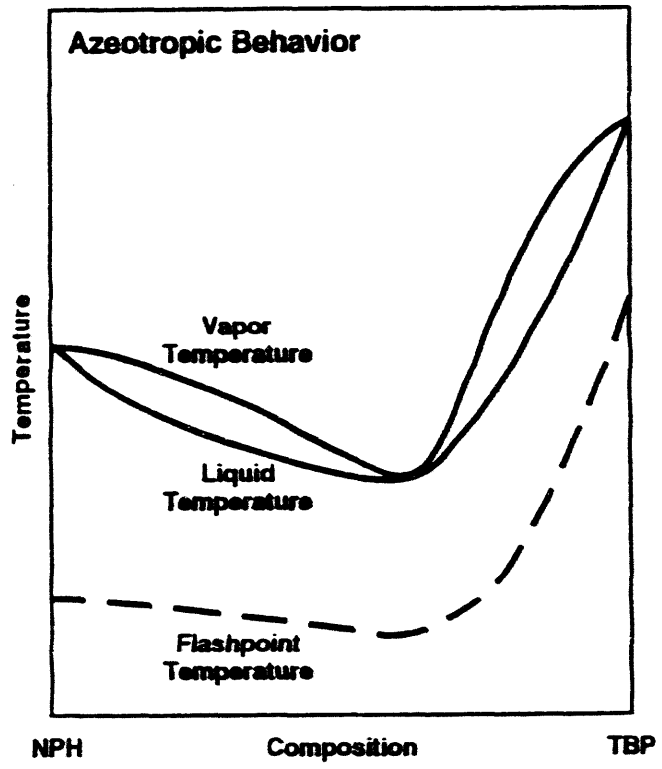
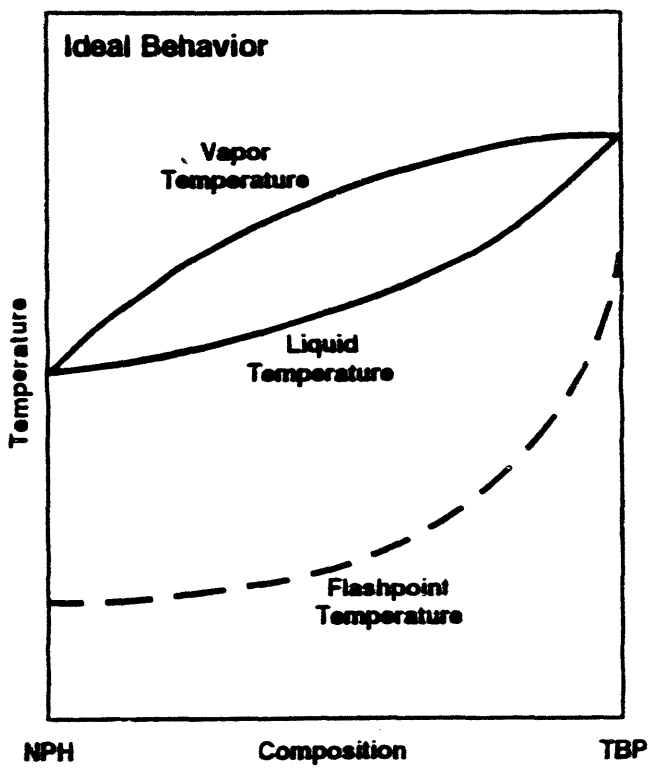
Table A-5. Observed Vapor Concentrations (mg/L) and Derived Activity Coefficients for C-103 Liquid Sample Vapors.

Compound	40 °C	70 °C	100 °C
Dedecane	0.32, 1.2	2.4, 1.3	13.8, 1.6
Tridecane	0.46, 1.7	4.2, 1.8	18.2, 1.5
Tetradecane	0.22, 4.2	1.2, 2.2	6.4, 1.9
TBP	0.14, 0.72	0.78, 0.57	8.4, 1.2

Using these non-ideal activities at 100 °C, the C-103 sample flashpoint is predicted to be 96 °C (205 °F). This is a minimum possible value, taking 150 °C for the TBP flashpoint and using the Table A-4 compositions.

A.6 POTENTIAL CHANGES OF THE C-103 ORGANIC LAYER FLASHPOINT

The flashpoint of the C-103 organic layer may change with time because of evaporative losses of individual compounds. Referring to Figure A-1, if the NPH-TBP mixture behaves nearly ideally, then volatile NPH components will preferentially evaporate, the remaining liquid will always become richer in TBP, and the flashpoint will increase with time. Note that according to Burger (1984) TBP is completely miscible with most organic solvents.



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Figure A-1. Hypothetical Liquid-Vapor Equilibria for NPH-TBP.

If the NPH-TBP mixture has an azeotrope, the same processes as in the ideal case will occur for mixtures richer in TBP than the azeotropic composition. For mixtures leaner in TBP than the azeotropic composition, vapors would actually be richer in TBP than NPH but again the flashpoint could only increase with time. Because measured vapors above the C-103 liquid sample are richer in NPH than TBP, while the sample itself is richer in TBP than NPH, it is clear that the C-103 layer behaves either like a nearly ideal system or like an azeotropic system richer in TBP than the azeotrope. In either case, the flashpoint of the mixture can only increase with time.

This conclusion may be independently confirmed by examining PNL data on NPH-TBP mixture flashpoints Pool (1994). Referring again to Figure A-1, near-ideal behavior is associated with a monotonic increase in the flashpoint as the higher boiling point component (TBP) is added to the lower boiling point component (NPH), and the flashpoint is skewed toward that of the lower boiling point component. An azeotropic system with positive deviations from ideality and a boiling point depression as illustrated would display weak variation in the flashpoint as the higher boiling point component is added until that component has a high mole fraction in the mixture; there may be a minimum in the flashpoint at the azeotrope. We may thus determine whether NPH-TBP systems conform to the ideal model by applying an ideal model and comparing the implied flashpoints with the data.

Although the exact composition of the NPH used by PNL is not known, the effective activity of all NPH compounds taken together may be judged using the PNL data. Deviations from ideality of TBP are moot due to its small vapor pressure and its negligible effect on the flashpoint for the TBP concentration of interest. The vapor pressure manifest by the NPH may be assumed to double approximately every 15 °C so the vapor pressure law for NPH in the vicinity of the flashpoint may be written as

$$P/P_o = 2^{(dT/15)} \quad (A-7)$$

where

- P = Vapor pressure
- P_o = Vapor pressure at the flashpoint
- dT = Temperature rise above the flashpoint of a pure NPH mixture

The vapor pressure manifest by NPH above a solution containing TBP may be assumed equal to P_o at the flashpoint of the solution because TBP contributes negligibly to flammability, therefore

$$P_o = P_x \quad (A-8)$$

where x is the mole fraction of NPH. Putting these together, if the solution behaves ideally, the flashpoint should rise with decreasing NPH concentration:

$$dT = -15 \ln(x)/\ln(2) \quad (A-9)$$

If the solution behaves nonideally, an activity coefficient, γ , for NPH may be found given measured dT and mole fraction pairs by replacing x with the product γx above:

$$1/\gamma = x 2^{(dT/15)} \quad (A-10)$$

Because the flashpoint of pure NPH measured by PNL was about the same as that of pure dodecane, the volume fraction of NPH cited by PNL may be converted to a mole fraction using formula weights of 170 and 266 for NPH and TBP respectively, and densities of 750 kg/m³ and 975 kg/m³ respectively. Applying this technique to the measured flashpoints yields the data in Table A-6 and Figure A-2.

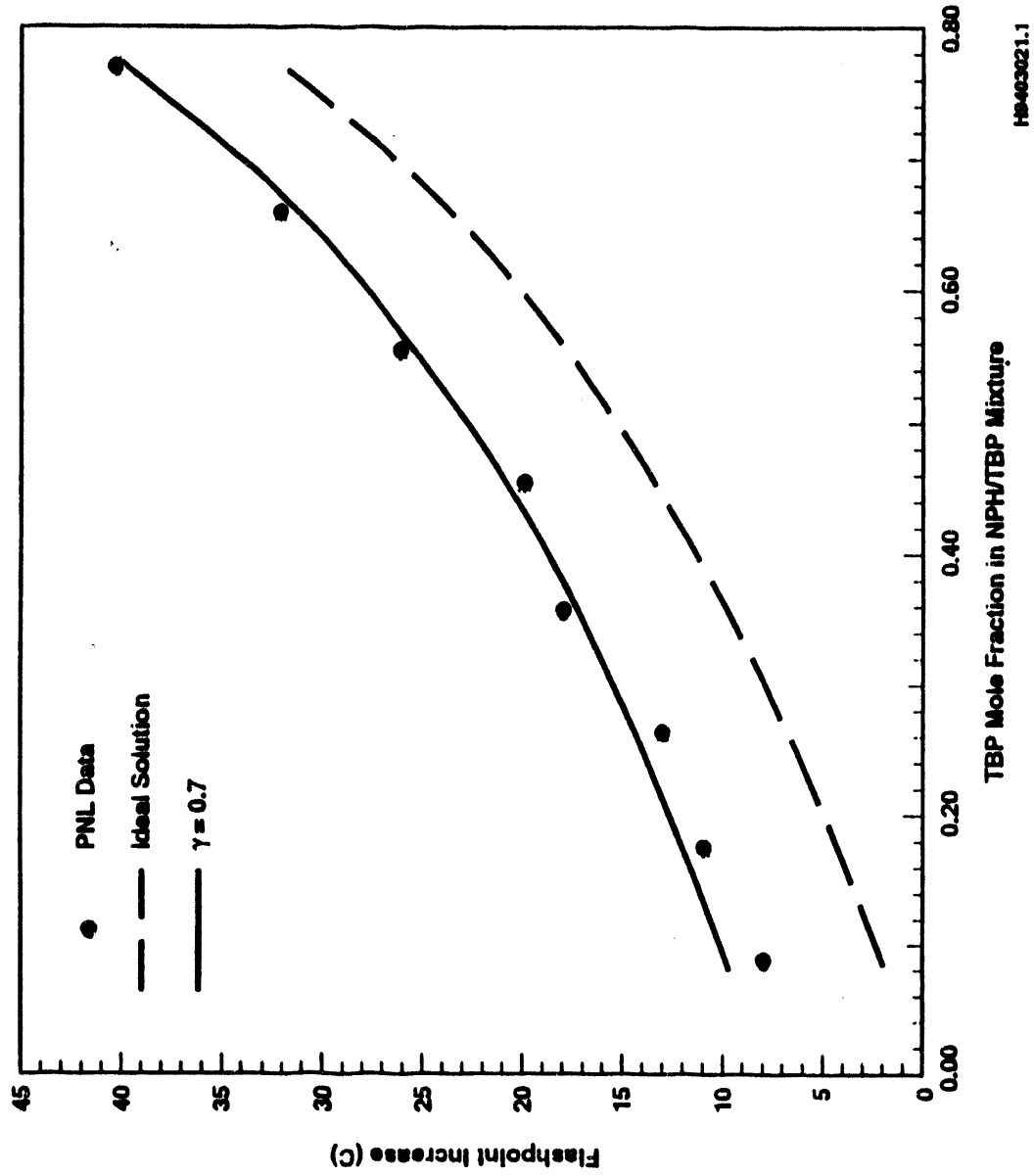
Table A-6, NPH-TBP flashpoint variation with composition, observed and calculated. "dT, PNL" is the measured increase in flashpoint with added TBP, "dT, ideal" is the ideal increase predicted by (3), and γ is the activity coefficient from (4) using x and "dT, PNL" data pairs.

Table A-6.

Vol% TBP	Mol% NPH	dT, PNL	dT, ideal	γ , implied
10	91.5	8	1.9	0.76
20	82.8	11	4.1	0.73
30	73.7	13	6.6	0.74
40	64.4	18	9.5	0.68
50	54.6	20	13.1	0.73
60	44.5	26	17.5	0.68
70	34.0	32	23.3	0.67
80	23.6	40	31.2	0.67

The resulting deviations from ideality are relatively small and consistent for the TBP-NPH system. The activities are below unity because the temperature difference for the flashpoint of pure NPH and a solution with 10% TBP, 8 °C, is much greater than the temperature

Figure A-2. Flashpoint Increase for TBP-NPH Mixtures with Added TBP.



difference of the flashpoints for the next 10% TBP increments, 3 °C to 5 °C. Even though the derived activity coefficients imply negative deviations from ideality, this process merely demonstrates that the NPH-TBP system behaves as expected using a near-ideal solution model.

Figure A-2 compares the flashpoint temperature rise measured by PNL with the calculations based on ideal behavior and employing a constant activity coefficient of 0.7. Clearly the flashpoint variation with composition behaves as expected for a nearly ideal system.

The long-term implication of this evaluation is that the flashpoint of the C-103 organic material is expected to monotonically increase as the material ages (i.e., as more volatile NPH low ends preferentially evaporate). Therefore conclusions drawn from the current measured flashpoint data and flashpoint calculations will be applicable in the future.

A.7 SUMMARY

The C-103 organic layer calculated flashpoint lies between 96 °C and 114 °C. The C-103 material behaves nearly ideally, exhibiting slight positive deviations from ideality which lower the calculated flashpoint below its ideal value. However, flashpoint data are consistent with ideal behavior. This flashpoint can only increase with time due to evaporative losses.

A.8 REFERENCES

- Burger, L.L. "Physical Properties" Science and Technology of Tributyl Phosphate Volume I, CRC Press, Boca Raton, Florida, 1984.
- Dean, J. A., 1985, Editor, "Lange's Handbook of Chemistry," 13th Edition, McGraw-Hill Book Company, New York, New York.
- Gerber, M. A., et al. September 1992, *Assessment of Concentration Mechanisms for Organic Wastes in Underground Storage Tanks at Hanford*, PNL-8339, AD-940, Battelle Pacific Northwest Laboratory, Richland, Washington.
- Kuchta, J. M., 1985, "Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries - A Manual," Bulletin 680, Bureau of Mines, U.S. Department of Interior, Washington, D.C.
- Pool, K. H. and R. M. Bean, 1994, PNL-94003, *Waste Tank Safety Project: Analysis of Liquid Samples from Hanford Waste Tank 241-C-1-3*, Pacific Northwest Laboratory, Richland, Washington.

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APPENDIX B
ADIABATIC CALORIMETRY OF C-103 ORGANIC LIQUID
LETTER NUMBER 9450575

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9450575

January 28, 1994

Dr. Roger M. Bean, Manager
Pacific Northwest Laboratory
Post Office Box 999
Richland, Washington 99352

Dear Dr. Bean:

ADIABATIC CALORIMETRY OF C-103 ORGANIC LIQUID

- References:
- (1) cc:Mail, Dr. R. M. Bean to Distribution, "RSST of C-103 Organic Liquid," dated December 8, 1993. (Attachment 3)
 - (2) D. B. Bechtold, September 16, 1991, "Laboratory Test Plan for Adiabatic Calorimetry of Single-Shell and Double-Shell Tank Waste," WHC-SD-WM-TP-104, Westinghouse Hanford Company, Richland, Washington.
 - (3) D. L. Herting, et al., August 20, 1992, "Laboratory Characterization of Samples Taken in December 1991 (Window E) from Hanford Waste Tank 241-SY-101," WHC-SD-WM-DTR-026, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

In response to Reference 1, this letter reports the results of adiabatic calorimetric analysis of a sample of organic liquid taken from Hanford waste tank 241-C-103. Results indicate the sample possesses a faintly perceptible self-heating tendency above 230 C when maintained as a liquid by high pressure. Subsequent general boiling completely tempers and absorbs this tendency. The final stages of unboiled residue decomposition yield only a small and short-lived self-heating event.

The sample was delivered to Process Chemistry Laboratories on December 16, 1993 bearing the identifier X-16. Three aliquots of the sample were analyzed as-is and without further treatment. The adiabatic calorimetry analyses were performed using a Fauske & Associates, Inc. RSST. The instrument and the procedures for its use are described in Reference 2, while the documentation of the tests is recorded in notebook number WHC-N-442-1. The methodology for interpreting each test result largely followed that described in Section 4.2 and Appendix B of Reference 3.

The instrumental output consists of computer-logged time, temperature and pressure data, which are graphed in various ways and interpreted. Five such graphs are Attached (Attachment 2) for each of the three analyses performed.

Dr. R. M. Bean
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Starting and ending values of temperature and pressure and weight are also read and recorded for the purpose of determining total production of noncondensable gas during an analysis. These and other calculated data are presented in the attached tables (Attachment 1).

A narrative interpretation of each sample analysis, based on these attachments, follows.

Test 931227

An aliquot of 9.89 grams was loaded into the sample holder along with a Teflon® stir bar and sealed in the RSST containment vessel. The containment was flushed three times by pressurizing to 400 psig with nitrogen followed by venting to ambient. Then 391 psig of nitrogen was added and containment was sealed for the run at a nominal heat rate of 1 C/min. Figure 1, Attachment 2 plots temperature, heater power and heater offset vs time for this test. Heater power is instrument-controlled to balance heat losses from the sample, and hence always rises with sample temperature, while the heater offset represents additional power added by the instrument only when the selected rate of temperature rise is not being achieved. Offset is generally triggered by endothermic events which depress the temperature rate, and once applied, is never removed, even when a sample subsequently increases the temperature rate by suffering a reduction in heat capacity or by undertaking to self-heat.

This particular run was terminated prematurely due to computer failure. Nonetheless, Figures 1 to 5, Attachment 2 show that nothing of consequence occurred in the sample until approximately 180 C, where a slight endothermic modulation of the heat rate brought on more heater offset. After that, an onset of general boiling occurred at 205 C, causing a rapid cooling of the sample and large increase in heater offset. Figure 2, Attachment 2 shows a drop in containment pressure corresponding to this cooling, as boil off and subsequent condensation at the containment walls acted to remove heat from the sample faster than the heater could provide it for about 20 minutes.

Figure 3, Attachment 2 reflects these events by showing a dip in the rate of temperature rise at the small endotherm and a large drop to negative values at the incidence of boiling. Figures 4 and 5, Attachment 2 are used to derive the actual uncondensed vapor production from the temperature and pressure data, removing the contribution of temperature increases from the pressure rise. The calculation is based on the assumption of steady state temperature gradients in the containment vapor phase, which temporarily loses validity during rapid temperature changes and large condensation events.

* Teflon is a trademark of E.I. Du Pont de Nemours and Company.

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The entries in Table 1, Attachment 1 for this test indicate that net gas production was so low it was actually exceeded by slow leakage (overnight) from the containment. The entries in Table 3, Attachment 1 based on these data confirm it. The calculations in Table 3 based on the logged data are less prone to slow leakage, and indicate a very sparse gas production. The net weight loss of the sample holder was due largely to boiloff of condensable solvent.

Nowhere in the test run is there any evidence of a self-heating event. The tabulated data of Tables 1 to 3, Attachment 1, for this sample also indicate that net gas generation was also very modest.

Test 931228

As shown in Figures 6 to 10, Attachment 2 this test was run at a slightly higher starting pressure of 398 psig nitrogen; otherwise the test parameters were substantially those of the previous run. Here, the slight endothermic modulation in temperature rate occurred at 230 C, and the sudden onset of general boiling at 298 C. In between, the increased offset caused by the endotherm recovered the temperature rate and increased it slightly to approximately 1.8 C/min, as shown in Figure 8, Attachment 2. On top of the increased rate, however, is a slight acceleration in rate which reached 3 C/min before being obliterated by the general boiling. This acceleration is interpreted as a self-heating event.

The boiling onset was caused by sudden bumping of superheated liquid, because the containment pressure at first rose rapidly before declining to a value reflecting transport of vapor to the cooler containment walls. The boiling called for a large increase in heater offset, which then drove the reduced liquid mass to higher temperatures at an increased rate of approximately 7 C/min, until another endotherm was encountered at 380 C.

After this second endotherm, it is clear that a sharp self-heating event was in progress by 400 C, which was exhausted by 430 C. An apparent general cooldown towards a lower temperature was the final event, caused most likely by there now being too little liquid or vapor left in the sample bulb to maintain thermal contact with the thermocouple. Post-test observations indicated no liquid was left in the bulb, rather it was condensed on the inside walls of containment and also soaked into the bulb insulation through a crack in the bulb. Only some char was left inside the bulb, and the stir bar was unrecognizable. Since the pre-test and post-test weights of the sample are based on a tare weight of bulb plus insulation, the quoted percentage weight loss in Table 1, Attachment 1 does not accurately reflect the loss of solvent which finds its way into the insulation.

The entries of Tables 1 and 3, Attachment 1 for this test indicate a modest total gas production. Figures 7, 9 and 10, Attachment 2 indicate that most of the production was associated with endothermic events.

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The two events assigned to self-heating for this test are characterized in Table 2, Attachment 1. The correction factor ϕ for organic liquid from tank C-103 is estimated to be 1.05, based on the specific heat of 0.47 for kerosene. Both events are apparently triggered by precursory endotherms, and both are small in extent.

Test 931229

This final test provided results similar to the preceding run, albeit at slightly different temperatures. Post-test examination of the sample revealed the same char and the absence of liquid in the sample bulb, which in this case, was intact. Again, there was organic condensate around the containment surfaces. As Figures 11 to 15, Attachment 2 show, the self-heat results are once again modest, so modest; in fact that the entries in Table 2, Attachment 1 suffer from lack of precision for both this and the previous test. It did not appear worthwhile to attempt to extract Arrhenius parameters for any of the self-heating events.

After three sample runs, the general conclusion reached by these analyses is that the C-103 organic liquid was not seen to self-heat below 230 C at high pressure, and that if it does, the temperature and gas production consequences are small.

Please do not hesitate to call me, if you have any questions on this matter.

Very truly yours,

D. B. Bechtold, Principal Scientist
Process Chemistry Laboratories
Facility Operations

dls

Attachments 2

RL - S. O. Branch
R. O. Puthoff (w/o attachments)

Table 1. C-103 Auxiliary Test Data.

Test ID	At start of run sample at ambient T			At end of run sample cooled to ambient T				Comment
	P _i (psig)	T ₀ (°C)	M ₀ (g)	P _f (psig)	T _f (°C)	M _f (g)	%ΔM (%)	
931227	391	19.9	9.89	386	17.1	9.17	-7.3	computer failure caused premature end
931228	398	18.6	9.38	419	22.6	7.06	-24.7	solvent in insulation decreases %ΔM
931229	402	18.9	8.98	425	26.1	6.52	-27.4	solvent in insulation decreases %ΔM

Table 2. C-103 Self-Heat Results.

Test ID	T _{max} (°C)	ΔT _{max} ^a (°C)	Max. dT/dt (uncorr.) (°C/min), at T (°C) ^a	Comments
931227	N/A	N/A	N/A	no self-heating evident
931228	240	φ x 8.6	φ x 3 C/min at 295 C	1st self-heat event
931228	400	φ x 19	φ x 45 C/min at 410 C	2nd self-heat event
931229	230	φ x 17	φ x 2.7 C/min at 290 C	1st self-heat event
931229	350	φ x 37	φ x 70 C/min at 385 C	2nd self-heat event

^aφ = 1.05

Table 3. C-103 Gas Production Results.

Test ID	F ^a	ΔM/M ₀ by calc. ^b (mol/g)	M _{gas} by calc. ^b (g/mol)	ΔM/M ₀ by auxiliary data ^c (mol/g)	M _{gas} by auxiliary data ^c (g/mol)
931227	0.1397	0.00034	212	-0.00054	---
931228	0.1466	0.0032	77	0.0014	176
931229	0.1409	0.0036	77	0.0012	228

units. ^a $PV = nRT_{\text{effective}}$, $T_{\text{effective}} = F \times T_{\text{sample}} + (1 - F) \times T_{\text{solvent}}$, $F = (dP/dT)_0 \times T_0/P_0$, in absolute
*Noncondensable gases only
*High because of (condensable) evolved solvent that contributes weight loss but not pressure.

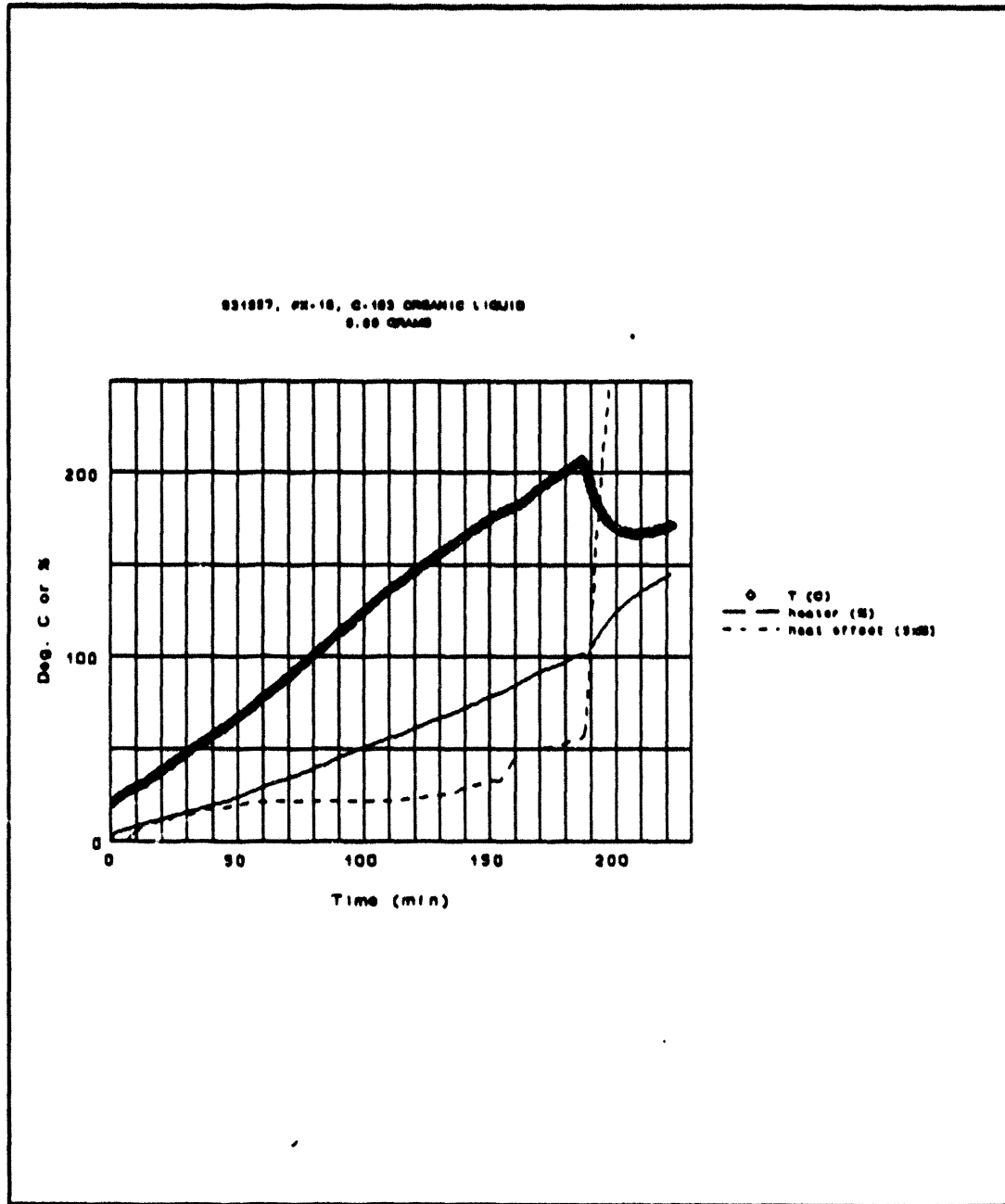


Figure 1

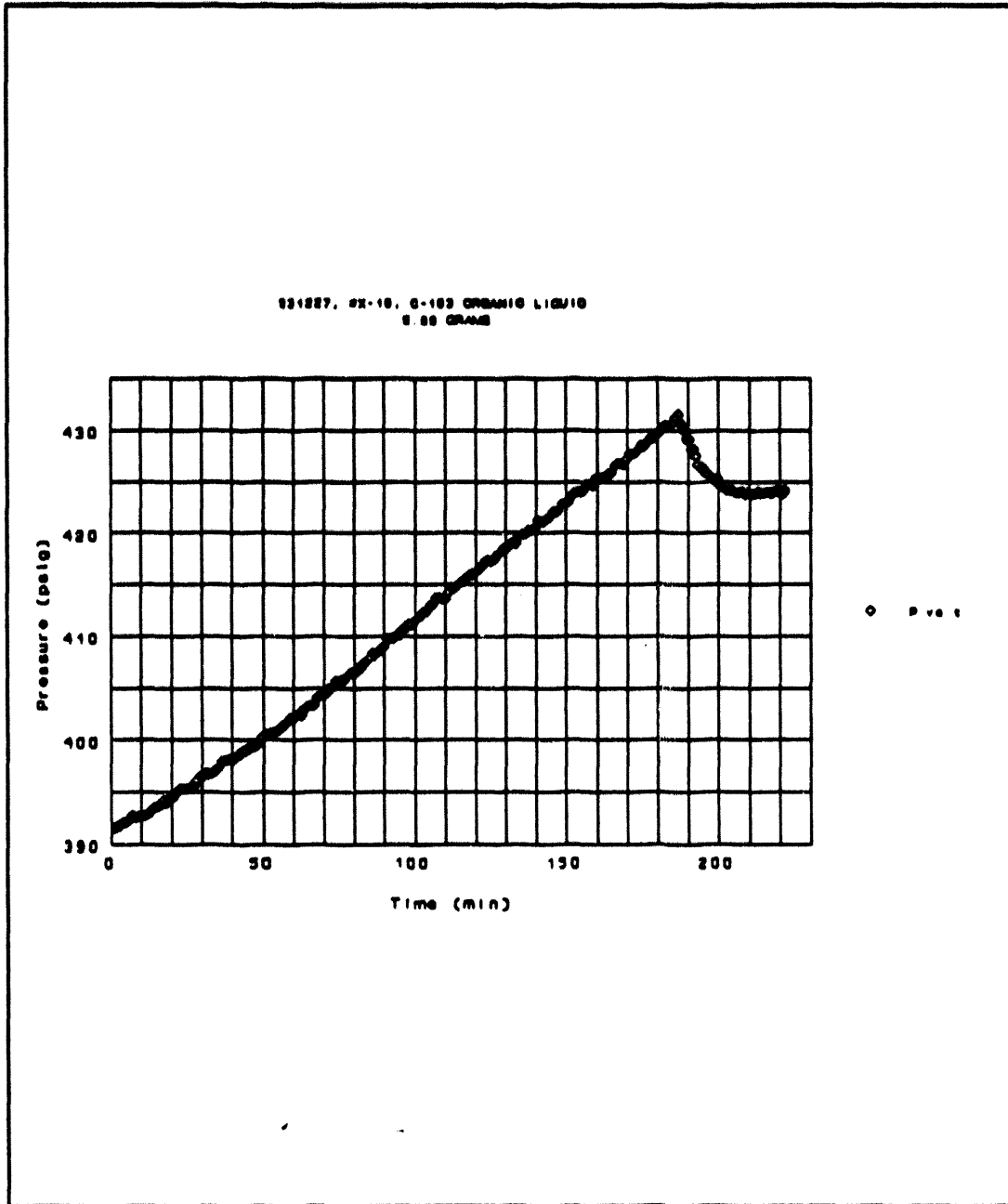
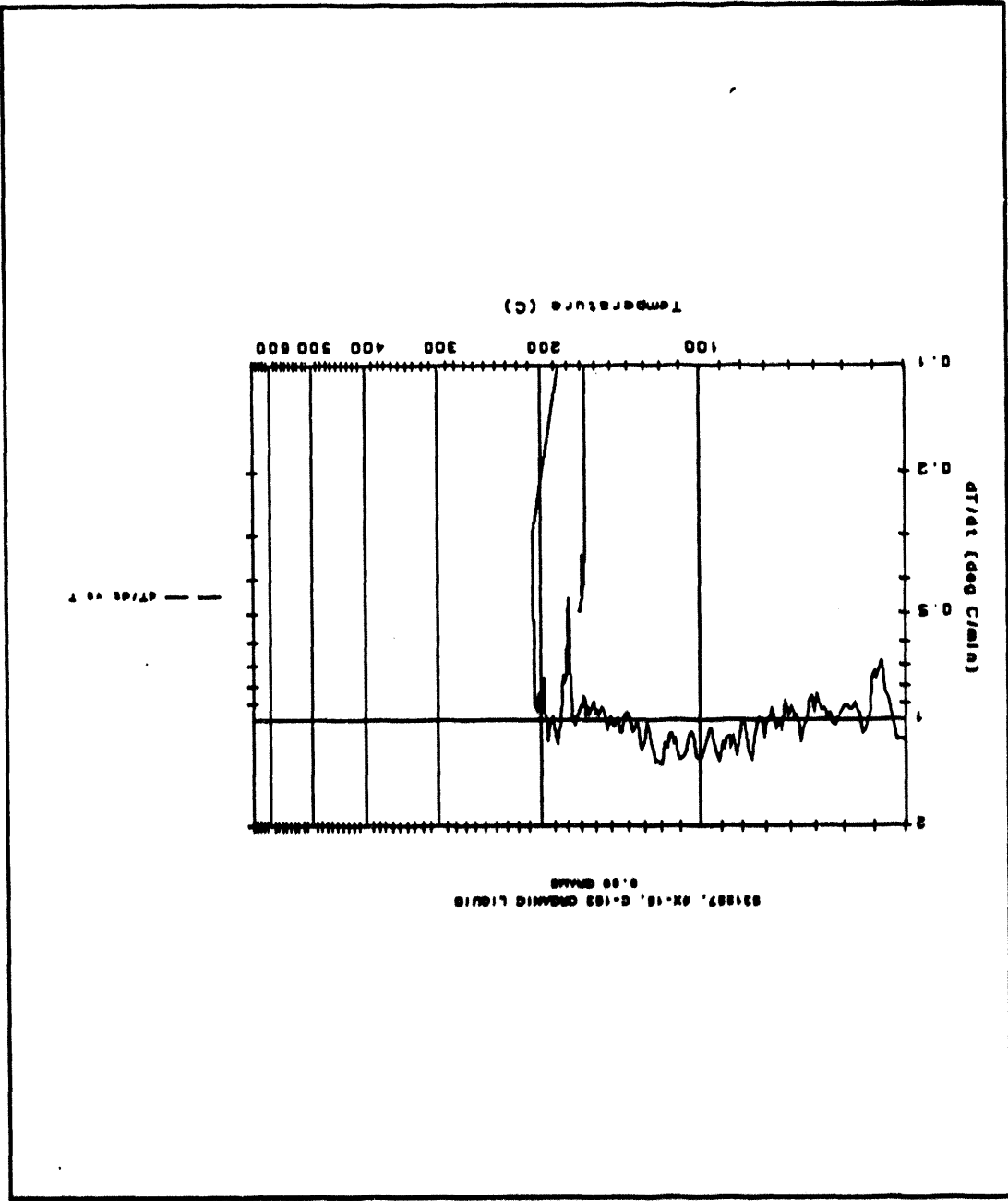


Figure 2

Figure 3



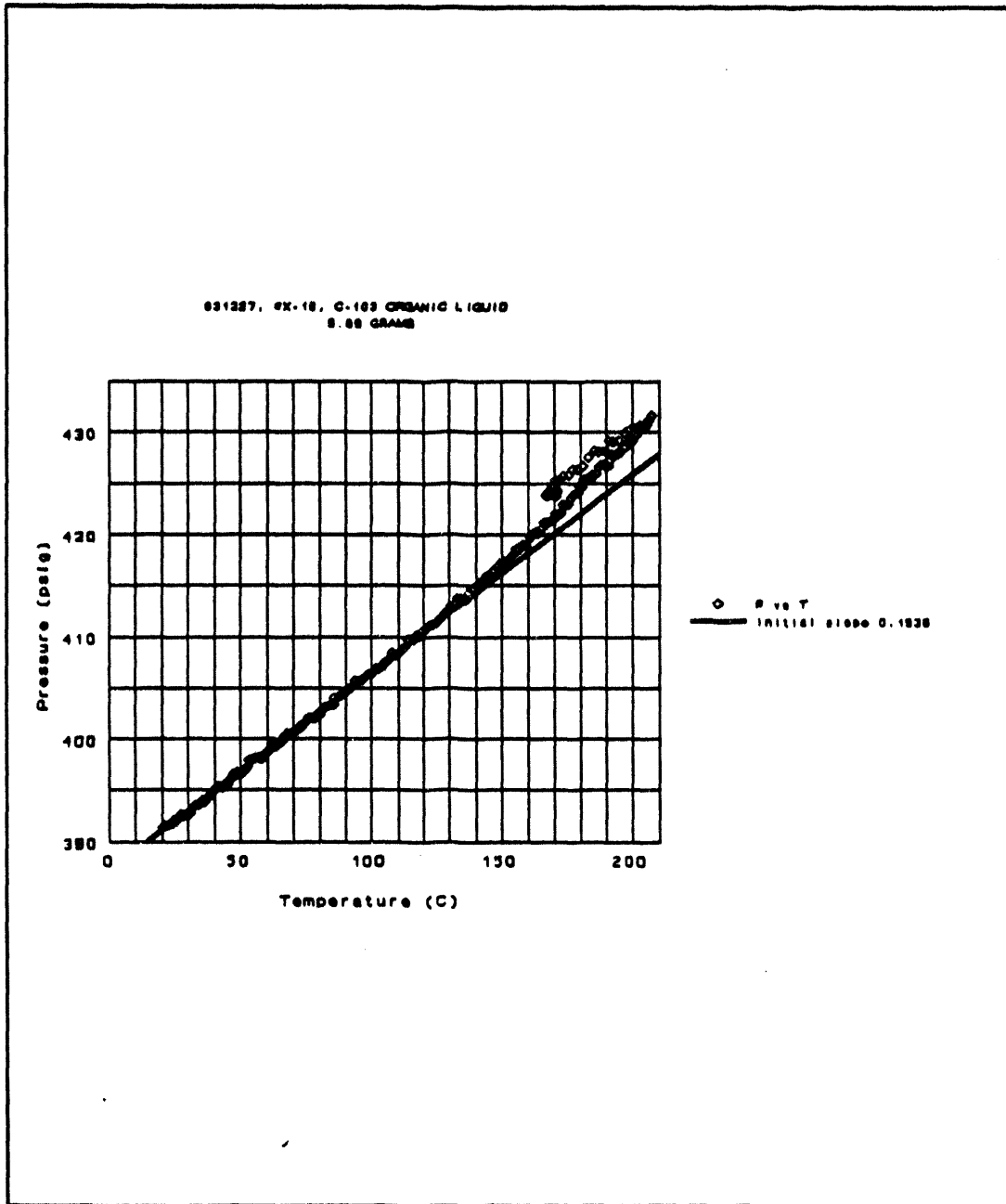


Figure 4

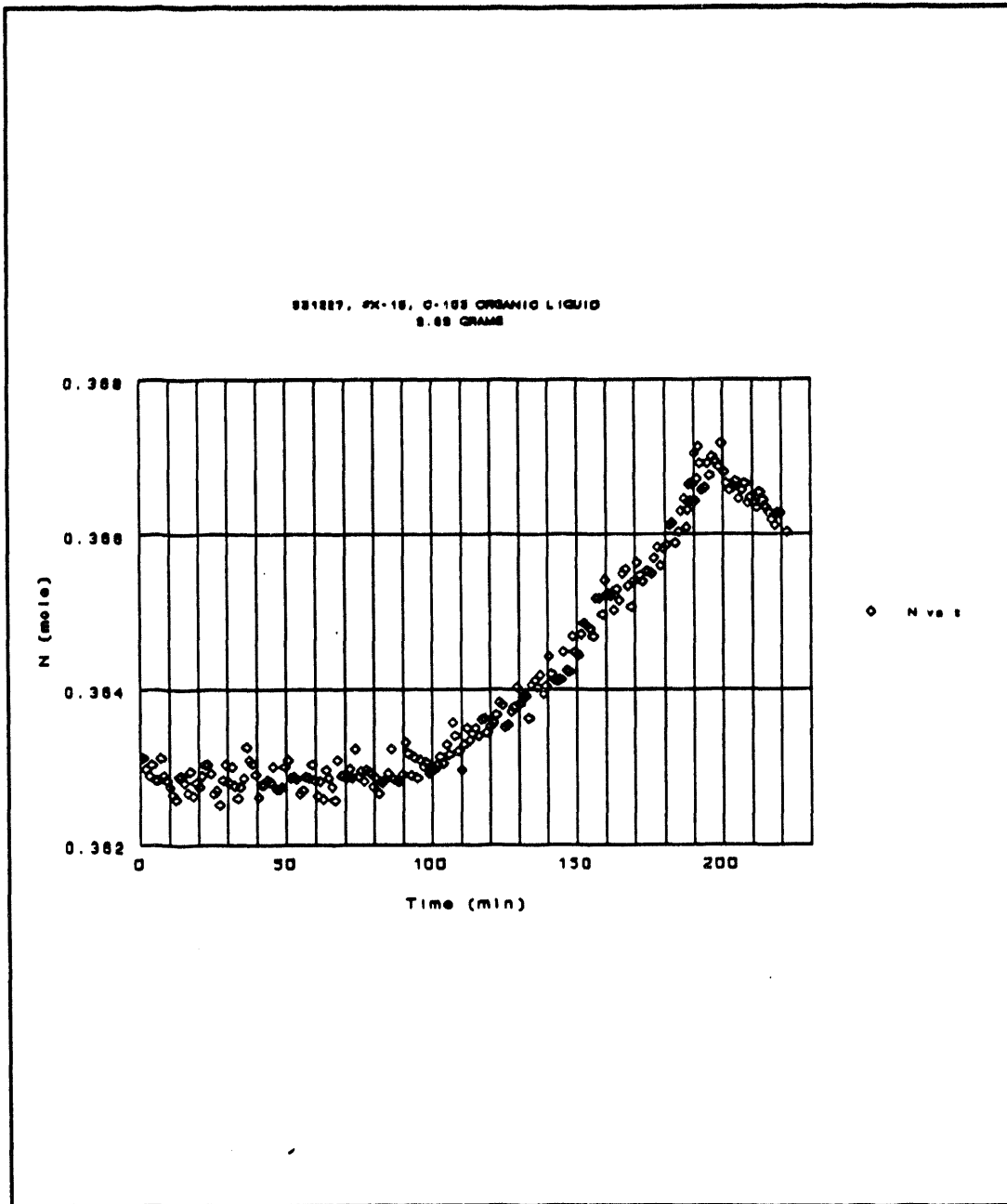


Figure 5.

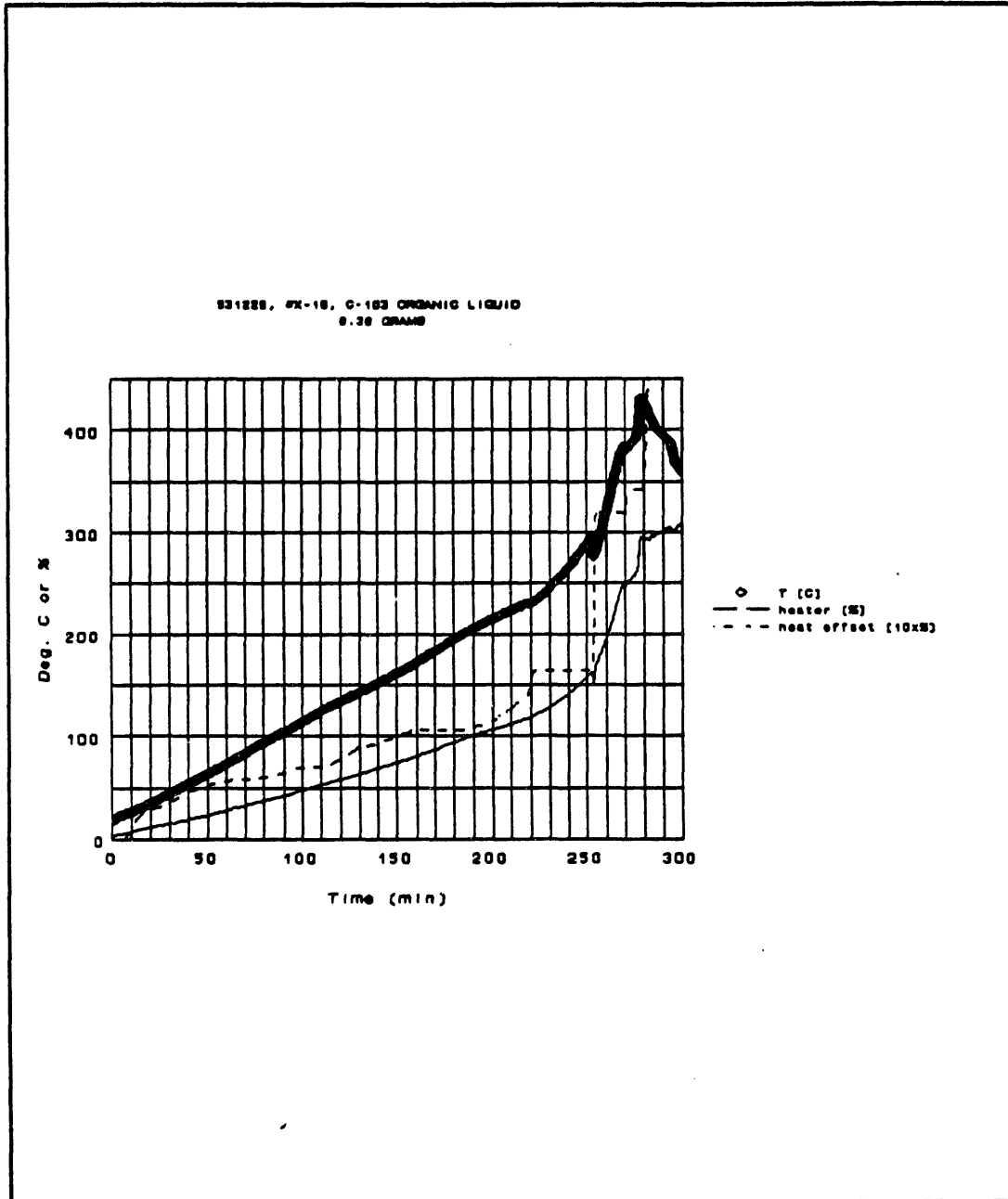


Figure 6

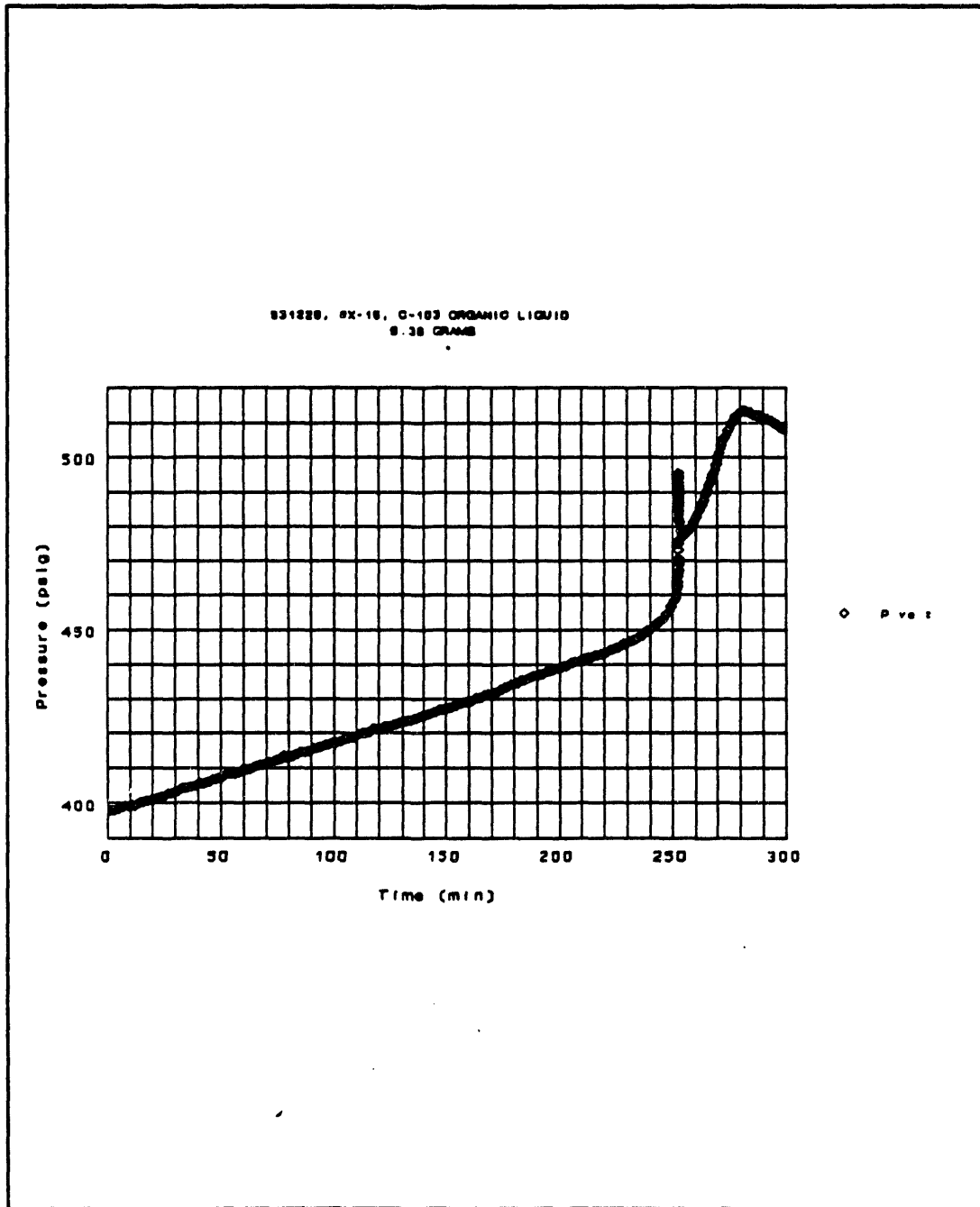


Figure 7

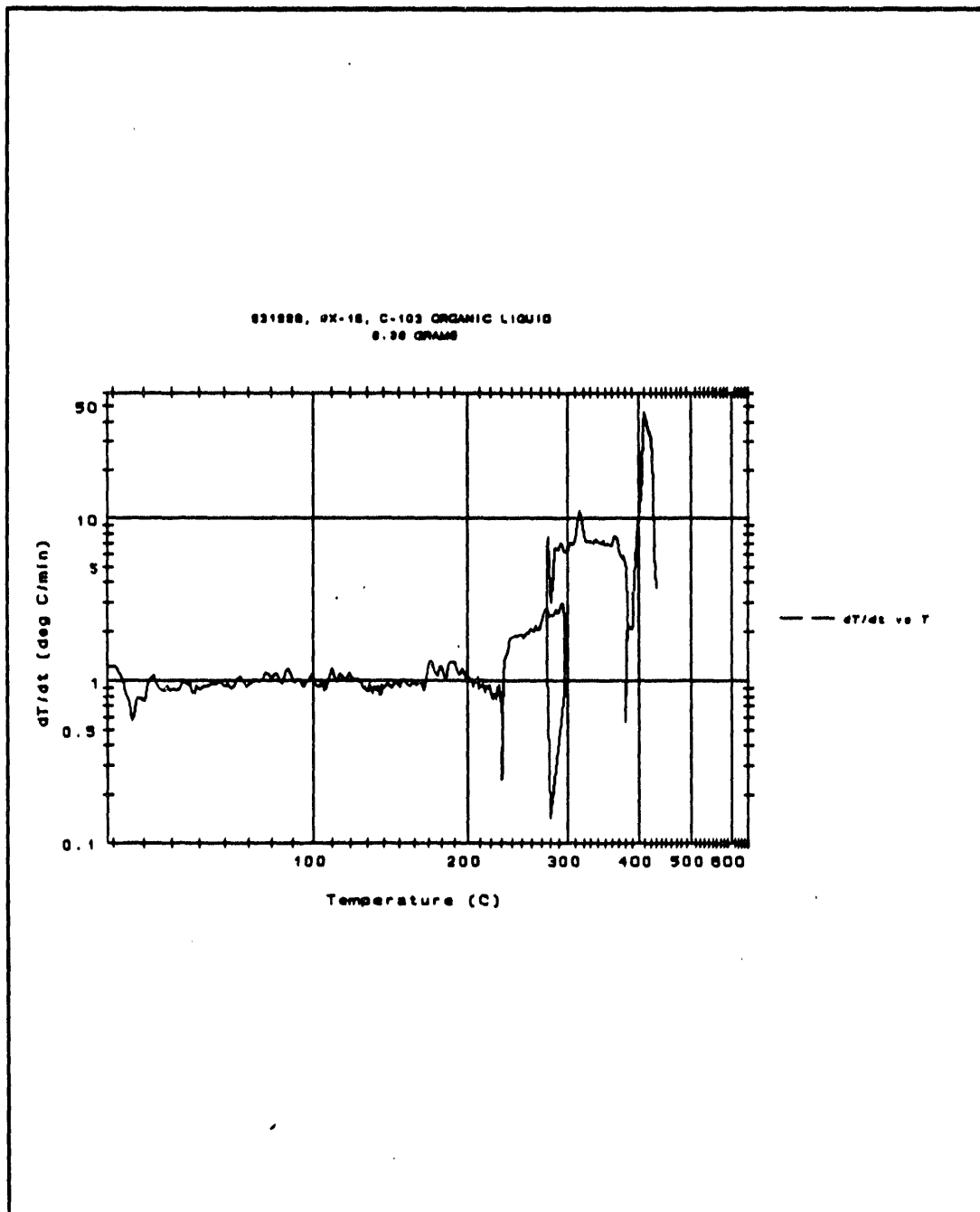


Figure 8

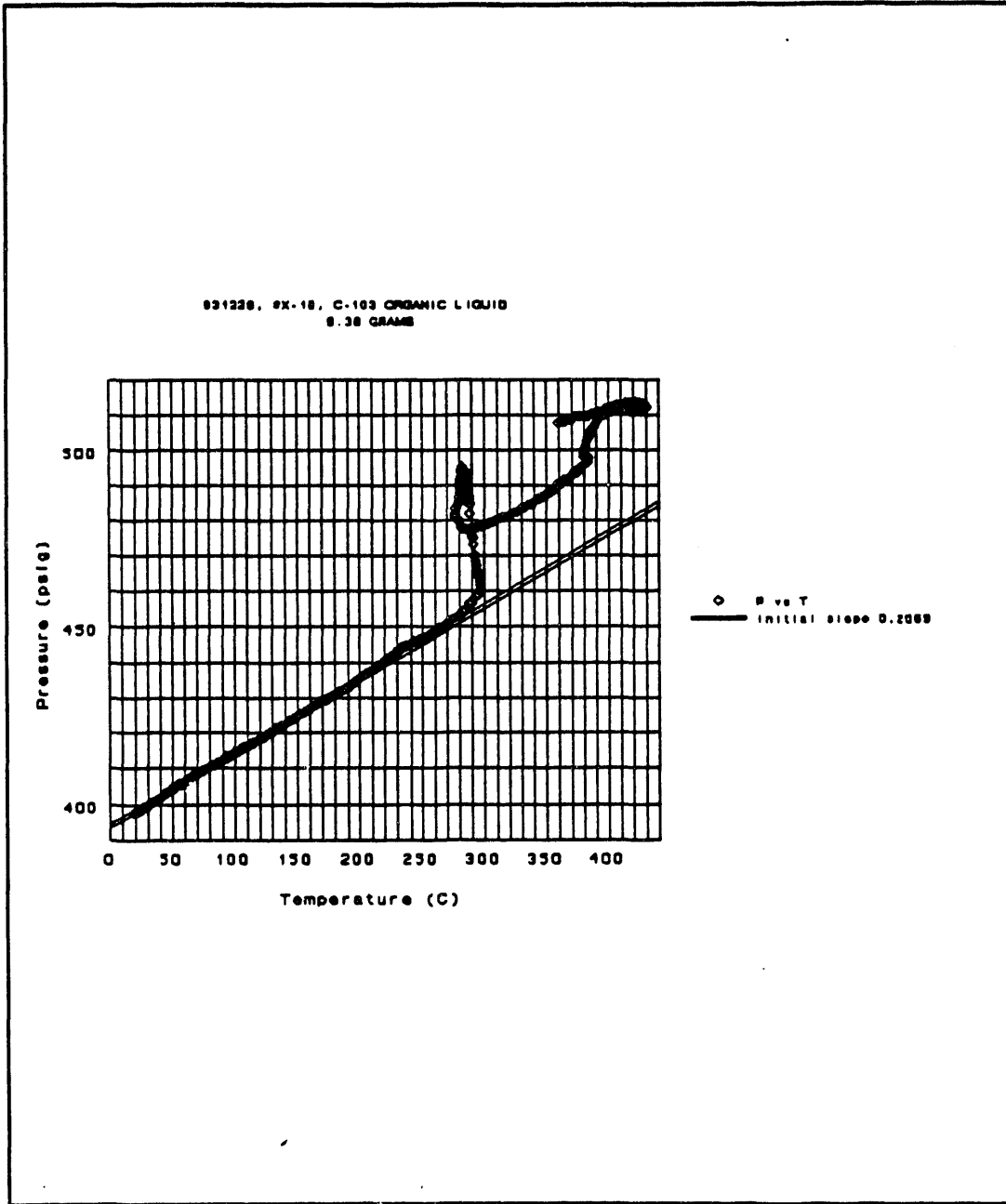


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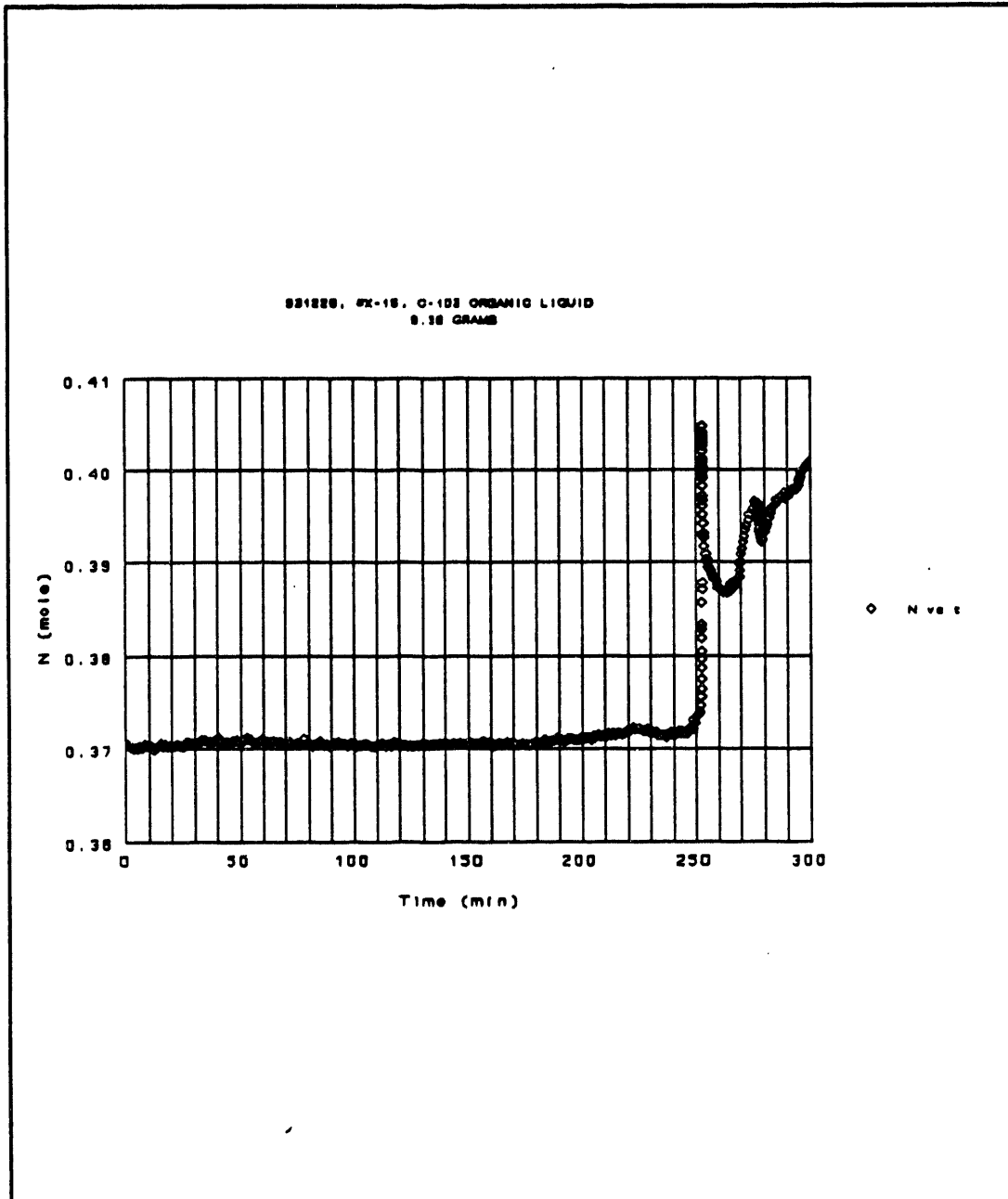


Figure 10

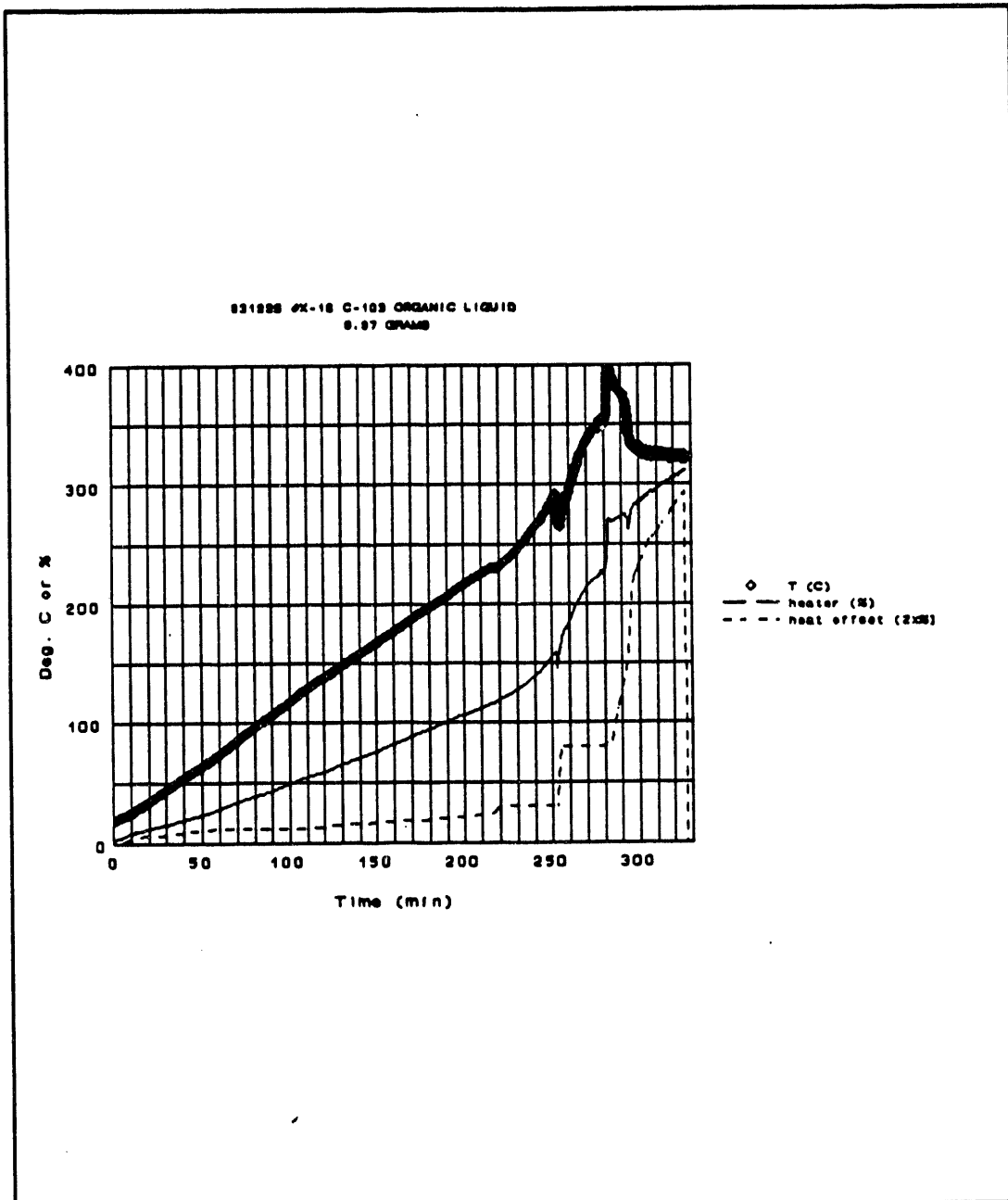


Figure 11

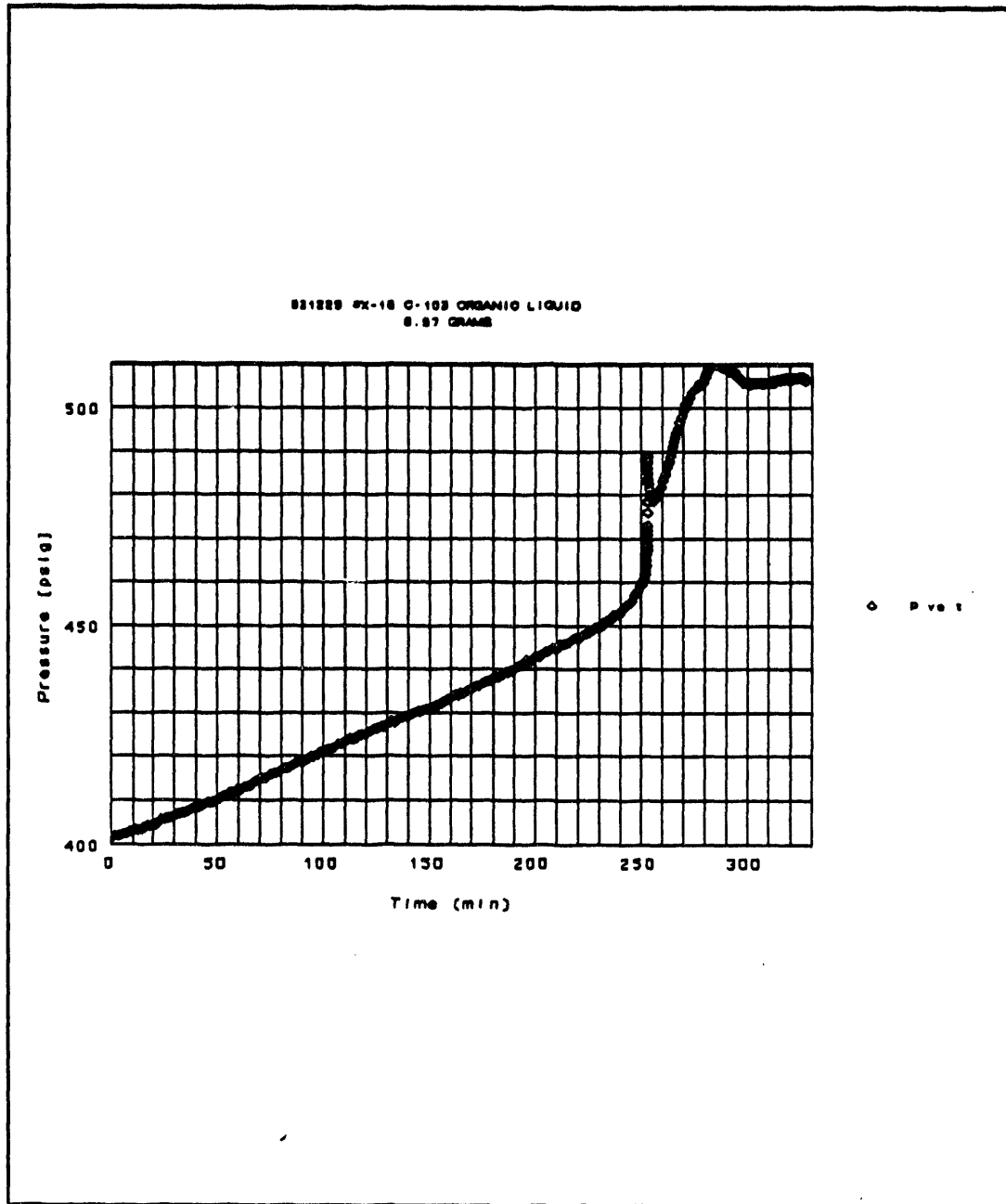


Figure 12

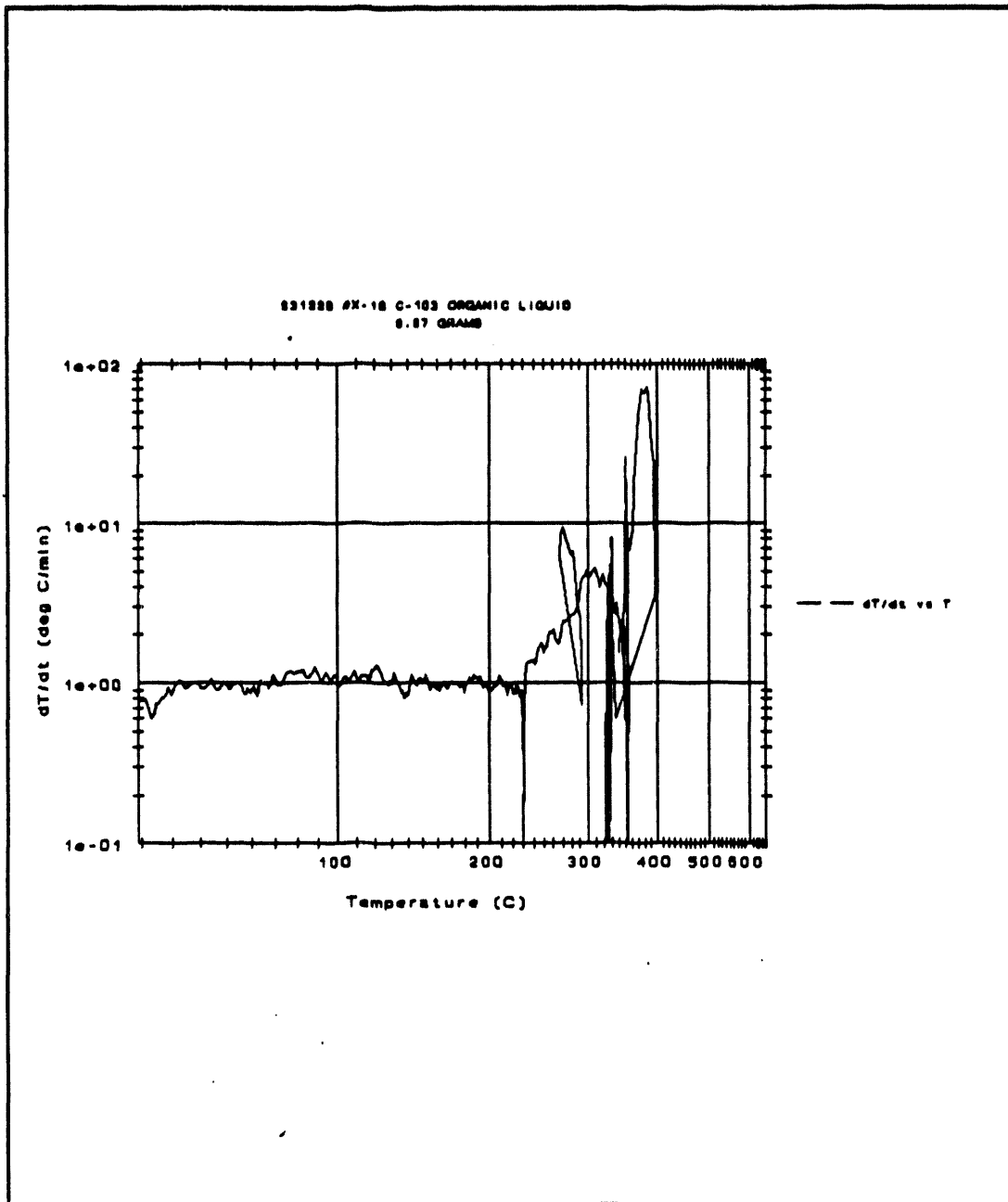


Figure 13

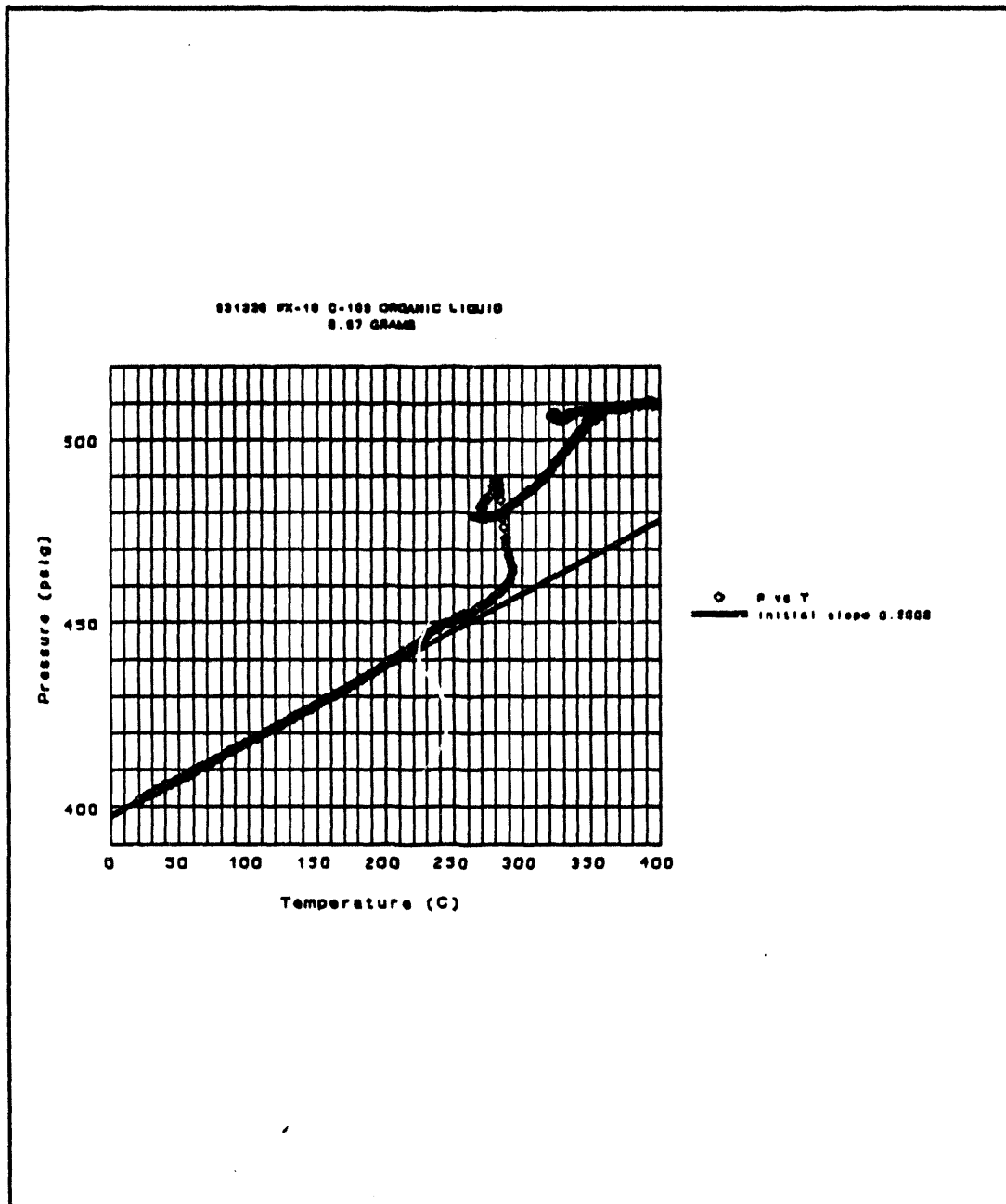


Figure 14

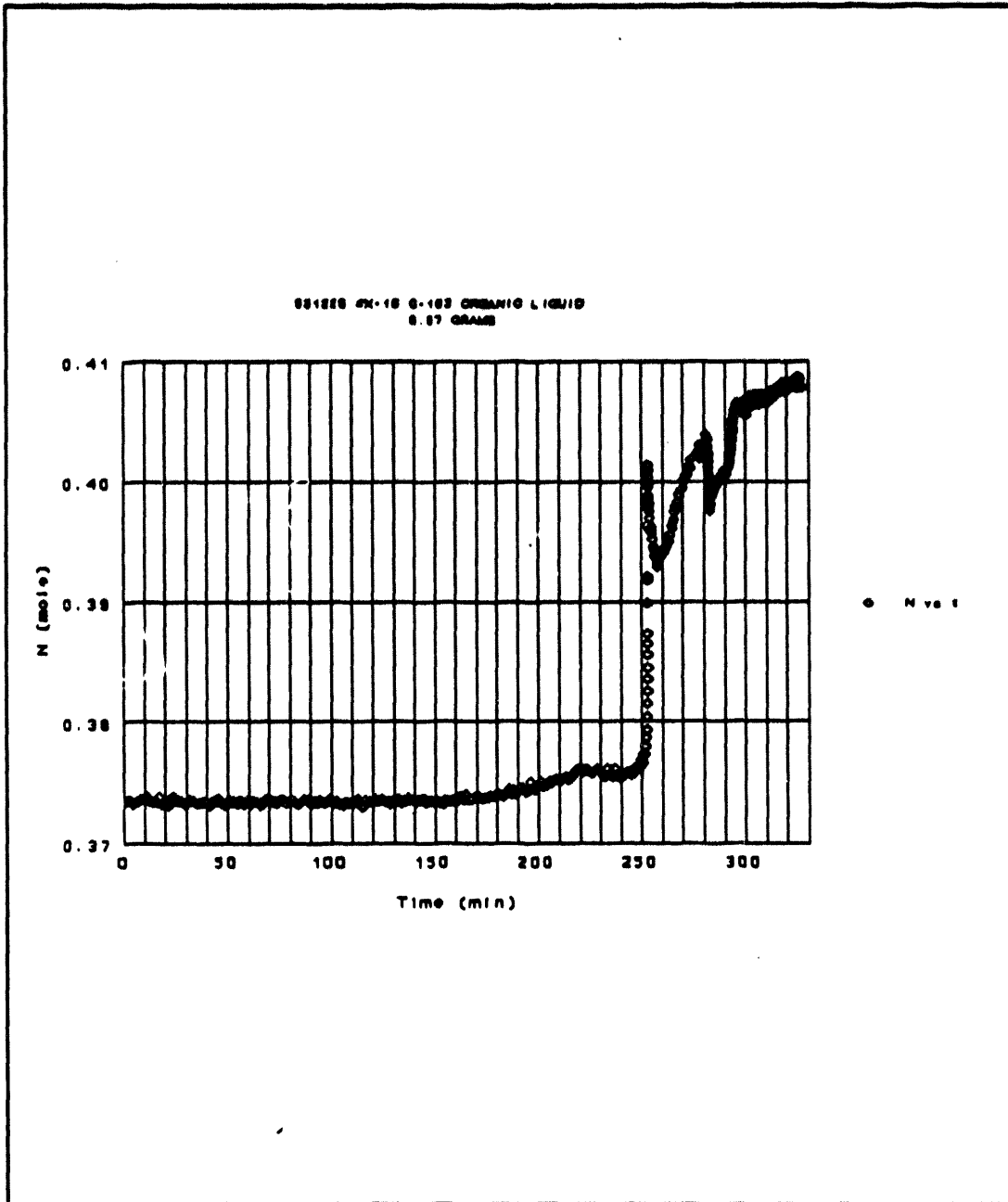


Figure 15

[13] From: Roger M Bean at ~PNL40 12/8/93 2:04PM (1310 bytes: 1 ln)
To: Marty G Plys at ~WHC150, David B (Dave) Bechtold at ~WHC168,
Randall D Scheele at ~PNL26, John M Grigsby at ~WHC150, Arlin K Postma at
~WHC150, David A Turner at ~WHC129, Karl H Pool at ~PNL56, Joel M Tingey at
~PNL26, James A Campbell
Subject: RSST OF C-103 ORGANIC LIQUID
----- Message Contents

After consultation with Randall Scheele of PNL, I have developed a tentative RSST test plan for the organic phase of C-103.

SAMPLES:

- 1) 10-mL duplicate runs of C-103 organic liquid, "as-is" from container.
- 2) 10-mL run of surrogate liquid consisting of TBP and NPH in the proportions determined from analysis.

CONDITIONS:

INITIAL TEMP = Room Temp
TEMP RATE = 1 deg/min
FINAL TEMP = LIMIT OF TEST APPARATUS

INITIAL CONDITIONS: Sample under nitrogen, in sealed system

PLEASE COMMENT ON THIS TEST PLAN. NOTE THE SERROGATE COMPARISON SAMPLE CANNOT BE PREPARED UNTIL AN APPROXIMATE ANALYSIS OF THE ORGANIC LIQUID IS OBTAINED BY GC/MS. LOGISTICS MUST BE DEVELOPED TO ENSURE THAT AT LEAST 25 ML OF SERROGATE IS PREPARED AND DELIVERED TO DAVE BECHTOLD IN A TIMELY FASHION.

THANK YOU

RM BEAN

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APPENDIX C
ANALYSIS OF CORE AND AQUEOUS SUPERNATANT
WASTE SAMPLES

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APPENDIX C

ANALYSIS OF CORE AND AQUEOUS SUPERNATANT
WASTE SAMPLES

C.1 ANALYSIS OF AQUEOUS SUPERNATANT SAMPLES

Duplicate samples of the aqueous supernatant liquid in tank C-103 have been analyzed for major components (Edrington 1991) and results are listed in Tables C-1 and C-2.

Inspection of the data of Tables C-1 and C-2 shows the solution to be mainly sodium nitrite and sodium sulfate at a pH of 9.5. The concentrations of nitrite and sulfate, expressed in terms of moles per liter amount to 0.7M and 0.3M respectively. As compared to many Hanford Site wastes, this solution is quite dilute, and is relatively high in sulfate.

C.2 ANALYSIS OF SLUDGE SAMPLES

The sludge in tank C-103 has been characterized by analysis of two push-mode core samples taken in 1986. Results are documented in the report of Weiss and Schull (1988).

Observation made during the sample unloading procedure are listed in Table C-3. Comparison of the two cores indicates that Core No. 1 contained solids over the bottom three segments (56 in.) whereas in Core No. 2, solids were present in only the lower two segments (37 in.). Also of interest is that relatively little organic liquid was recovered in the top segment. If the volumes of organic and aqueous liquids recovered are assumed to be proportional to depth, then Core No. 1 indicates the organic liquid depth to be $11.2 \text{ in.} \times 8/102 = 0.88 \text{ in.}$ and Core No. 2 indicates the depth to be $12 \text{ in.} \times 25/181 = 1.66 \text{ in.}$ These depths inferred from core samples are significantly smaller than the depth inferred from the volume of organic liquid thought to have been pumped from tank C-102 (~13-in. based on 36,000 gal).

The depths of organic liquid indicated by the 1986 core sampling effort (0.88 in. and 1.66 in.) are of the same magnitude as the depth (1.5 in. to 2 in.) measured in a recent sampling effort (Huckaby 1994).

Risers R-2 and R-8 are both roughly 5 ft from the wall of the tank but are on opposite quadrants. Riser R-2, is located near the thermocouple tree on the southern quadrant. The tank bottom at these two risers is roughly 11.5 in. above the centerline bottom. Adding segment lengths for each sample listed in Table C-3 and then adding 11.5 in. to account for bottom slope, waste depth is calculated to be 6.56 ft and 6.63 ft for Cores No. 1 and No. 2 respectively. These values agree well with the value based on level measurement, 6.52 ft, as reported by Hanlon (1993).

Sludge depths estimated from segments that contained solids (Table C-3 data) amount to 56 in. and 37 in. for Cores No. 1 and No. 2 respectively. These depths are greater than the 30 in. indicated by a sludge level measurement (Hanlon 1993).

The sludge volume of 62,000 gal reported by Hanlon (1993) was computed from a level measurement, using a volume of 12,500 gal for the conically-shaped bottom portion of the tank and a volume per foot of 33,050 gal/ft for the cylindrical portion of the tank.

These three estimates of sludge depth are significantly different and indicate that sludge depth varies with position. Likewise, supernatant liquid depth would vary: for a sludge depth of 57 in., supernatant liquid is calculated to be $6.52 (12) - 57 = 21$ in. For a sludge depth of 30 in., supernatant liquid depth is calculated to be $6.52 (12) - 30 = 48$ in.

Selected radionuclide concentrations for core composite samples, as reported by Weiss and Schull (1988) are presented in Table C-4. A comparison of results for the two cores indicates that drainable liquids from the two cores have similar nuclide concentrations. The solids in Core No. 1, on the other hand, have nuclide concentrations that are roughly double those of Core No. 2.

Table C-1. Cation Concentration in Aqueous Supernatant Liquid (Edrington 1991).

Cation	Sample number		Average	Cation	Sample number		Average
	R8108	R8109			R8108	R8109	
Na ppm	36,000	36,000	36,000	Fe ppm	4	4	4
Zr ppm	300	290	295	Ca ppm	3	3	3
K ppm	270	260	265	Cu ppm	3	2	2
Cr ppm	81	77	79	Mg ppm	2	2	2
Ni ppm	80	76	78	Cd ppm	1	1	1
Ag ppm	24	24	24	Mn ppm	0.3	0.2	0.2
Si ppm	22	21	21.5	As mg/L	0.12	0.12	0.12
Mo ppm	12	12	12	Se mg/L	0.03	0.03	0.03
Al ppm	10	9	10	Hg ppm	<	<	<
Sn ppm	5	5	5				

< = Value less than detection limit for sample matrix.

Table C-2. Analysis of Aqueous Supernatant Liquid From Tank C-103 (Edrington 1991).

Analysis	Sample number		Average
	R8108	R8109	
%H ₂ O	91	91	91
TOC (g/L C)	7.46	7.44	7.45
pH	9.5	9.5	9.5
Specific gravity	1.07	1.06	1.06
Anions			
OH ⁻ M	▲	▲	▲
NO ₂ ⁻ ppm	30,000	27,000	28,500
NO ₃ ⁻ ppm	4,300	4,200	4,250
CO ₃ ⁻ M	0.4	0.4	0.4
SO ₄ ⁻ ppm	26,000	27,000	26,500
PO ₄ ⁻ ppm	2,100	2,000	2,050
Radiochemistry			
Total Beta μCi/L	82,000	94,000	88,000
GEA-liq μCi/L	74 Co-60 64,000 Cs-137	67 Co-60 62,000 Cs-137	70.5 Co-60 63,000 Cs-137
Sr-89/90 μCi/L	2,500	3,300	2,900
Tc-99 μCi/L	37	67	52
Pu-239/40 μCi/L	24	24	24
Am-241 μCi/L	0.3	0.5	0.4

▲ = pH too low to make OH⁻ determination.

Table C-3. Physical Observations of Core Samples From Tank C-103 (Weiss and Schull 1988).

Core No.	Segment No.	Radiation reading (mrad)	Segment length (in.)	Description of solids	Weight solids (g)	Description of liquids	Weight liquid (g)
1*	1*	170	11.2	No solids	0	94 ml aqueous 8.0 ml organic	118.24
1	2	1300	19	Dark brown/black margarine-like	272.56	No liquid	0
1	3	1700	19	Similar to Segment 2 but not as soft	122.60	107 ml	
1	4	800	18	Mostly brown/black small portion white	263.63	11 ml	
2**	1	200	12	No solids		25 ml organic 156 ml aqueous	187.72
2	2	250	19	No solids		132 ml aqueous	141.41
2	3	1400	19	Dark brown runny	296.47	49 ml aqueous	
2	4	400	18	Mostly white/firm 20% dark brown	281.36	15 ml aqueous dark brown	

*Taken from Riser R-2.

**Taken from Riser R-8.

* Segment No. 1 is at top of waste.

Table C-4. Radiochemical Analysis of Core Composite Samples From Tank C-103
(Weiss and Schull 1988).

Nuclide*	Concentration in core composite samples			
	Solids, $\mu\text{Ci/g}$		Liquids, $\mu\text{Ci/L}$	
	Core 1	Core 2	Core 1	Core 2
Pu-239,40	1.90 E+01	1.25 E+01	3.37 E+01	3.37 E+01
Sr-90	4.16 E+03	1.66 E+03	1.95 E+03	2.63 E+03
Tc-99	4.67 E-01	1.96 E-01	3.70 E+01	3.57 E+01
Am-241	< 1.57 E+00	< 1.44 E+00	< 3.74 E+00	< 1.31 E+00
Cs-137	1.39 E+02	7.70 E+01	2.21 E+04	2.12 E+04
Total gamma	2.26 E+02	1.05 E+02	2.22 E+04	2.13 E+04

*Measurement date of May 8, 1987.

Nuclide concentrations in drainable liquids extracted from core samples would be expected to be similar to concentrations in aqueous supernatant liquids. A comparison of liquid concentrations presented in Table C-4 with those of Table C-2 generally shows good agreement between the two independent data sets. The largest discrepancy involves Cs-137: core samples are low by roughly a factor of 3 compared to supernatant. No explanation for this discrepancy is evident.

The bulk density of solids in the composite prepared for Core No. 1 was reported as 1.18 g/ml and for Core No. 2 it was 1.54 g/ml. Drainable liquid had densities of 1.11 g/ml and 1.08 g/ml respectively for Cores 1 and 2.

C.3 REFERENCES

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Hanlon, B. M., February 1993, *Tank farm Surveillance and Waste Status Report for November 1992*, WHC-EP-0182-56, Westinghouse Hanford Company, Richland, Washington.

Huckaby, J. L., 1994, "Field Report for collection of Liquid Samples from Tank 241-C-103 on December 15, 1993," Internal WHC Memo, from J. H. Huckaby to J. W. Osborne, 7A300-94.003, dated February 2, Westinghouse Hanford Company, Richland, Washington.

Weiss, R. L. and K. E. Schull, 1988, *Data Transmittal Package for 241-C-103 Waste Tank Characterization*, SD-RE-TI-203, Westinghouse Hanford Company, Richland, Washington, January 8, 1988.

APPENDIX D

**PREDICTED CONCENTRATIONS OF ORGANIC AEROSOLS IN THE
VAPOR SPACE OF TANK C-103**

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APPENDIX D

PREDICTED CONCENTRATIONS OF ORGANIC AEROSOLS IN THE
VAPOR SPACE OF TANK C-103

D.1 SUMMARY AND CONCLUSIONS

The MAEROS-2 computer code (Gelbard 1982) was used to estimate the maximum expected concentrations of organic liquid aerosol in the dome space of Tank C-103. The tank vapor space was modeled as a single closed volume, with a specified mass rate of aerosol particles released into it. The code calculated the removal rate of droplets by settling and plateout.

Figure D-1 shows the predicted aerosol mass concentration in the dome space over time for three different aerosol production rate assumptions. The middle curve represents a production rate of 1.2 mg/s (.0096 lb_m/hr). This is the predicted rate of aerosol formation from heterogeneous nucleation in a saturated atmosphere minus the expected condensation rate on ceiling and walls. This value was calculated assuming an organic liquid mixture that is approximately 73 mass percent tributyl phosphate, and 27 mass percent normal paraffin hydrocarbons. Concentrations were also calculated for formation rates one order of magnitude above and below the predicted rate.

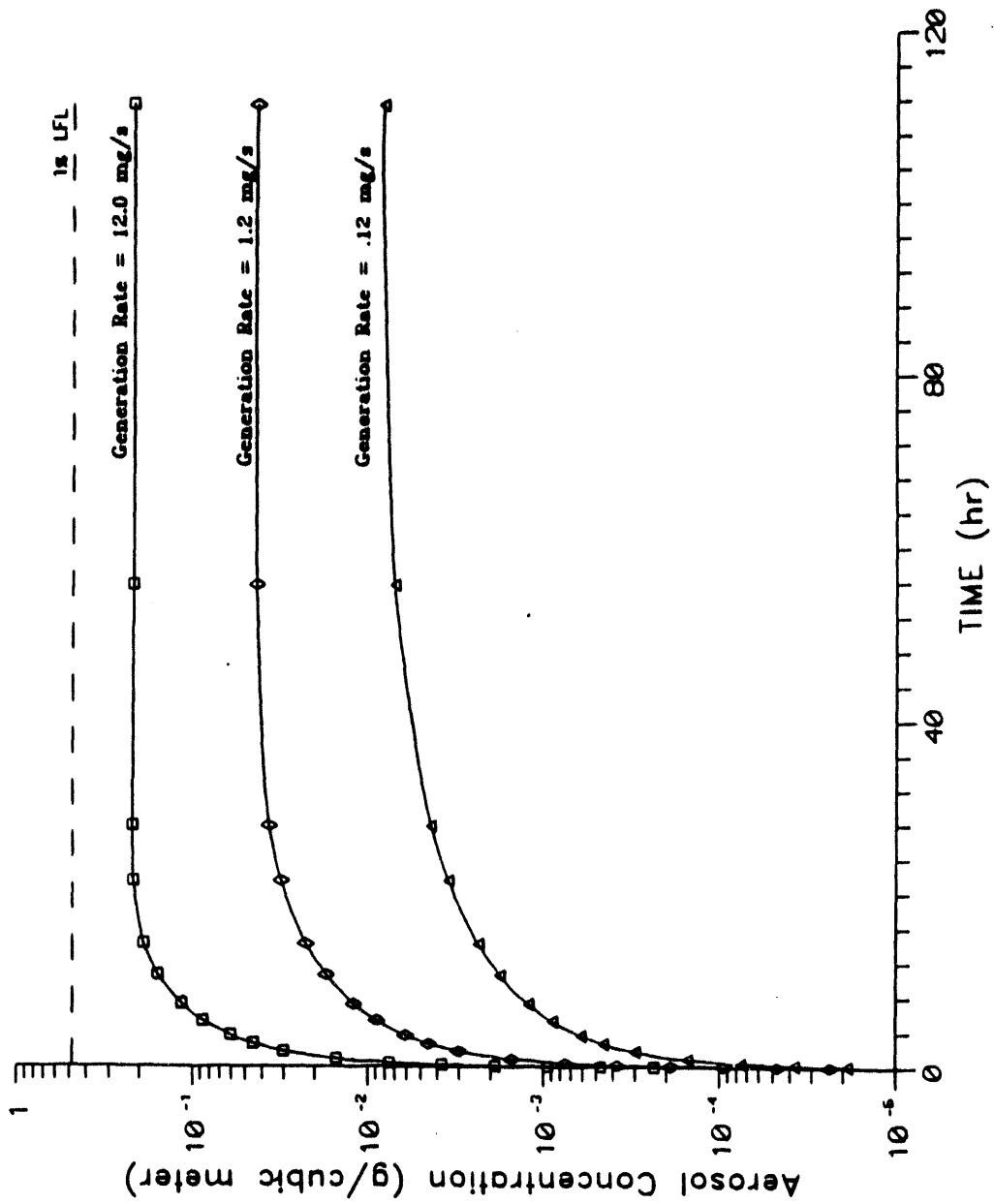
The curves show that the maximum predicted concentration of aerosols to the tank atmosphere (for the liquid composition specified in Table D-2) is about 43 mg/m³. This is less than 0.1% of the lower flammability limit (45 to 50 g/m³) for normal paraffin hydrocarbons (Zabetakis 1965). Therefore it is concluded that, under conditions thought to apply to Tank C-103, aerosols formed in an atmosphere saturated with organic vapor do not significantly increase the potential for creating a flammable mixture.

D.2 VAPOR SPACE MAXIMUM AEROSOL CONCENTRATION

D.2.1 AEROSOL FORMATION

A conservative estimate of the maximum generation rate of organic aerosols in the tank vapor space was calculated. It was assumed that the tank atmosphere was everywhere saturated with organic vapor originating from the surface of the pool. Aerosol droplets were assumed to be formed by condensation from this saturated atmosphere onto small particles present in the atmosphere.

Figure D-1. Predicted Peak Concentrations for Organic Aerosols in Tank C-103.



The evaporation rate of the organic species from the pool into a saturated atmosphere was calculated for an assumed temperature difference of 1.11 °C (2 °F) across a small boundary layer at the liquid-air interface. The steady state rate of mass transfer through this boundary layer is proportional to the concentration difference across it.

$$N_A = k_e(C_L - C_v) \quad (D-1)$$

where:

N_A = Mass transfer rate (lb_m/h ft²)

k_e = Mass transfer coefficient (ft/h)

C_L = Equilibrium concentration of vapor at liquid surface temperature (lb_m/ft³)

C_v = Equilibrium concentration of vapor at temperature on vapor side of boundary layer (lb_m/ft³).

The equilibrium concentration of the vapor as a function of temperature was obtained by applying Raoult's Law. This specifies that, for a mixture of chemically similar liquids, the partial pressure of each component in a vapor at equilibrium with the liquid is approximated by multiplying the liquid phase mole fraction of that component by the vapor pressure, at the given temperature, of that component in a pure state. Mass concentration of each component in the vapor was calculated from partial pressures using the ideal gas law. The values for all components were added to obtain the total mass concentration of vapors.

The composition of one batch of NPH used at the Hanford Site, along with molecular weights and vapor pressure constants, are listed in Table D-1.

Table D-1. Properties of NPH.

Component	MW	Mole fraction ^a	A ^b	B ^b	C ^b
Decane, C ₁₀ H ₂₂	142.3	0.039	6.94365	1495.17	193.86
Undecane, C ₁₁ H ₂₄	156.3	0.328	6.97220	1569.57	187.70
Dodecane, C ₁₂ H ₂₆	170.3	0.286	6.99795	1639.27	181.84
Tridecane, C ₁₃ H ₂₈	184.4	0.219	7.00756	1690.67	174.22
Tetradecane, C ₁₄ H ₃₀	198.4	0.129	7.013	1740.88	167.72

^aComposition from Beary (1970).

^bVapor pressure constants from Dean (1985).

The constants A, B, and C listed in Table D-1 are so-called Antoine constants that correlate vapor pressure to temperature according to the following equation.

$$\log_{10}P = A - B/(T+C) \quad (D-2)$$

where:

P = Vapor pressure, mmHg
T = Temperature, °C.

Constants that apply to TBP were derived from its normal boiling point (289 °C) and its vapor pressure at 60 °C of 0.1 mmHg (Gerber et al. 1992). For TBP the molecular weight is 266.32 and the vapor pressure constants A, B, and C were derived to be 8.527, 3173, and 273.16 respectively.

Evaporation of the more volatile components during the 20+ years of storage would change the composition of the NPH-TBP mixture. The present composition of a TBP-NPH mixture initially composed of 30% by volume TBP and 70% by volume NPH (Table D-1 composition) was computed for a fractional volatilization process that was based on the following key assumptions.

1. Raoult's law applies, so the vapor pressure of each component is given by the mole fraction times its vapor pressure.
2. The density of NPH and TBP are 0.76 g/ml and 0.975 g/ml respectively (Moore and Walser 1980).
3. The present NPH-TBP mixture is composed of 73% by weight TBP and 27% NPH (Prentice 1991).
4. Vaporization took place at 45 °C (113 °F).
5. Vapor pressure suppression of organic species due to the presence of dissolved water was neglected.
6. Radiolytic and other chemical reactions were neglected.

The predicted present composition of the organic layer and partial pressures of the organic molecular species present are presented in Table D-2.

Table D-2. Predicted Present Composition of Organic Liquid.

Component	Mole fraction	Partial pressure (mmHg)
C ₁₀ H ₂₂	1.0 E-16	0.5 E-15
C ₁₁ H ₂₄	5.98 E-06	1.01 E-05
C ₁₂ H ₂₆	1.14 E-02	6.73 E-03
C ₁₃ H ₂₈	0.134	2.64 E-02
C ₁₄ H ₃₀	0.194	1.31 E-02
TBP	<u>0.661</u>	<u>2.37 E-02</u>
	1.000	6.99 E-02

A review of the data of Table D-2 shows that the lighter fractions have been mostly stripped, leaving C₁₃H₂₈, C₁₄H₃₀, and TBP as the main components. The partial pressures add to a total of 0.0699 mmHg, which amounts to a volume percent (in air at 743 mmHg pressure) of 0.009%. When compared to the LFL for the main organic species present (approximately 0.6%) volatile organic liquid species are predicted to amount to only 1.6% of the LFL.

For the predicted present composition of the organic layer in Tank C-103, as given in Table D-2, the equilibrium concentration of vapors at 45 °C (C_L) is 4.73 x 10⁻⁵ lb_m/ft³. The concentration at 43.9 °C (C_v, 2 °F lower) is 4.327 x 10⁻⁵ lb_m/ft³.

Analogies between heat and mass transfer, applicable at low mass transfer rates, have been derived. One of these, the Chilton-Colburn analogy (Sherwood et al. 1975) gives an expression for estimating the mass transfer coefficient, k_c.

$$k_c = \frac{hD_{AB}}{k} \left(\frac{Sc}{Pr} \right)^{1/3} \quad (D-3)$$

where:

- h = Heat transfer coefficient (Btu/h °F ft²)
- k = Thermal conductivity (Btu/hr °F ft), 0.016 for air
- D_{AB} = Diffusivity of organic in air (ft²/h)
- Sc = Schmidt number, dimensionless
- Pr = Prandtl number, dimensionless, 0.7 for air.

The temperature difference of 1.11 °C (2 °F) was based on an analysis of decay heat dissipation in Tank C-103. Details of the analysis are described in Appendix F.

The heat transfer coefficient, h , was evaluated from an equation (McAdams 1954) that applies for natural convection to air from a heated horizontal plate facing upward.

$$h = 0.22 \Delta t^{1/3} \quad (D-4)$$

where:

Δt = Temperature difference (2 °F).

This gives a predicted value for h of 0.28 Btu/hr ft² °F.

An estimation for the diffusivity of organic in air, D_{AB} , was based on the assumption that tetradecane would represent the volatile species. Empirical relationships for calculating the diffusivity of gases and vapors are given in standard handbooks (Perry 1950). The calculated value for tetradecane in air is 0.216 ft²/h. The Schmidt number was calculated to be 3.1.

Therefore,

$$k_c = \frac{0.28 \frac{BTU}{hr \cdot ft^2 \cdot ^\circ F} \times 0.217 \frac{ft^2}{hr}}{0.016 \frac{BTU}{hr \cdot ft \cdot ^\circ F}} \left(\frac{3.1}{0.7} \right)^{1/3} = 6.2 \frac{ft}{hr} \quad (D-5)$$

and

$$N_A = 6.2 \frac{ft}{hr} (4.73 \times 10^{-5} - 4.33 \times 10^{-5}) \frac{lb_m}{ft^3} = 2.5 \times 10^{-5} \frac{lb_m}{ft^2 \cdot hr} \quad (D-6)$$

When this is multiplied by the surface area of the liquid pool, 4418 ft², the mass transport rate into the vapor space from the pool is .11 lb_m/hr (0.0139 g/s).

It was assumed that a certain amount of the condensation that takes place from the saturated vapor would occur on the cooler dome and exposed wall area of the tank. This condensate, as it forms, would create a film on those surfaces and eventually run off back into the liquid pool. Therefore, it does not contribute to the aerosols present in the vapor space.

The method described above was used to calculate the rate of condensation on the dome. The calculation was conservative in that the available area for condensation was taken to be the cross sectional area of the tank (4418 ft²). The additional area provided by the convex shape of the dome and by the exposed wall surface was neglected.

The temperature difference across the boundary layer was again taken to be 1.11 °C (2 °F). The temperature on the vapor side of the boundary layer was assumed to be 43.9 °C and on the dome side, 42.8 °C. The calculated rate of condensation was 0.100 lb_m/hr. The total aerosol formation rate is then 0.0096 lb_m/hr (0.00121 g/s).

D.2.2 AEROSOL REMOVAL

As the aerosol droplets form in the vapor space, they are subject to various forces that cause them to be in motion. As they move, they encounter and interact with other aerosol particles, as well as with available surfaces. As the concentration of particles in the air increases, the frequency of this interaction increases. When droplets contact each other, they will adhere together and combine their mass. As heavier droplets are formed, the gravitational force pulling them downward increases, overcoming upward drag forces to a greater degree. Eventually, an equilibrium is reached at which the fallout rate is comparable to the generation rate. Additional removal from the aerosol population occurs when a particle collides with a solid surface and adheres to it.

D.2.3 CALCULATION OF EXPECTED AEROSOL CONCENTRATIONS IN THE VAPOR SPACE

A conservative estimate of the maximum expected aerosol concentration in the vapor space of Tank C-103 was postulated as the concentration achieved at equilibrium between aerosol formation in and removal from the control volume. Removal mechanisms were limited to those described in the previous paragraph, i. e., coagulation and gravitational settling, and plateout on surfaces. Other mechanisms for deposition (thermal deposition, concentration driven diffusion through boundary layers, and others) were ignored. The MAEROS-2 computer code was used to calculate the expected vapor space concentration over time until equilibrium was reached.

D.2.3.1 The MAEROS-2 Computer Code

The MAEROS code was developed at Sandia National Laboratories in the 1970's to analyze aerosol transport in reactor containment systems following hypothetical accidents. The aerosol particles are distributed in sections, or bins, according to size. The mass and number of particles in each size bin are updated at each time step as agglomeration and removal processes change the size distribution.

The code models were validated in the early 1980's by comparison with the results of aerosol tests performed by the Hanford Engineering Development Laboratory (HEDL) (Hilliard 1984). This testing program, called ABCOVE, was undertaken for the purpose of evaluating the adequacy of aerosol behavior computer codes. Both MAEROS and the CONTAIN code (Murata 1985), which incorporates MAEROS for its aerosol behavior modeling, produced results for aerosol concentrations and size distributions that compared very well with the test results.

MAEROS-2 is a stand alone version of the code, compiled to run on a personal computer with a DOS operating system. This PC version was obtained from Dr. Fred Gelbard, Sandia National Laboratories, who controls the distribution of the code and maintains a list of authorized users. Operation of the code was tested prior to its use for these calculations, both by running the test case that was provided with the code, and by attempting to duplicate the results of a case that had previously been modeled using CONTAIN on the Cray computer. As expected, the test case gave identical results to those provided.

The case previously modeled with CONTAIN represented a glove box, initially loaded with 100 mg/m^3 of plutonium oxide aerosols of less than 10 micrometers diameter. Gravitational settling and deposition on surfaces, and remaining aerosol concentration in the cell were calculated for a period of 20,000 seconds. MAEROS-2 predicted aerosol concentrations within 1% of those calculated by CONTAIN at times less than 1000 seconds. Thereafter, the MAEROS-2 results were generally higher than those from CONTAIN, with a deviation of about 11% at 20,000 seconds.

This difference can be accounted for by the fact that the CONTAIN model provided a breach in the glove box. This allowed the glove box to "breathe" after its pressure equalized with that in the adjoining room. As a result, small amounts of aerosol left the cell and were not recovered. This effect was not incorporated in the MAEROS-2 model. Therefore, it was concluded that, considering this slight difference in the modeling, the MAEROS-2 results are consistent with those calculated by CONTAIN.

D.3.2 MAEROS MODEL FOR TANK C-103 VAPOR SPACE

Three cases were run. All input for each of the three cases were identical, except that the aerosol mass source rate was varied. For the initial case, the mass source rate was taken to be 1.2 mg/s ($.0096 \text{ lb}_m/\text{hr}$). This is the aerosol production rate as calculated in Section D.2.1. Two additional cases, with aerosol source rates of $.12 \text{ mg/s}$ and 12.0 mg/s were also calculated to bracket the potential uncertainty in the aerosol formation calculation.

The tank vapor space was modeled as a single closed volume of 2560 m^3 . The vapor space gas was modeled as air at a constant 317.0 K and one atmosphere pressure. The material density of the aerosol droplets was given as 906 kg/m^3 . This is the estimated density of a liquid mixture that is 73 mass percent TBP and 27 mass percent NPH. The initial aerosol

concentration in the volume was taken to be zero. The aerosols were assumed to form at a constant rate throughout the duration of the run until a steady state concentration was reached. The aerosol formation was assumed to occur uniformly throughout the volume, so that the distribution of aerosols was everywhere the same at all times.

The sizes of the aerosol droplets, as they formed, were assumed to be log-normally distributed with diameters ranging between 0.10 and 10 micrometers. The geometric mass mean diameter was 0.13 micrometers and the geometric standard deviation 2.0. The MAEROS-2 input file for the 1.2 mg/s source term is reproduced as Table D-3. An abbreviated version of the output file for the same case is given in Table D-4. It summarizes the physical parameters and initial conditions and gives the mass balance, aerosol concentration, and particle size distribution at 800,000 seconds (222 hours).

The calculated aerosol concentrations in the volume over time for the three cases are shown in Figure D-1. In all cases the aerosol concentration increases as the aerosol formation rate exceeds the rate at which mass is removed by gravitational settling and deposition on available surfaces. After some time, a steady state is reached where the production rate and the removal rate are approximately equal. After this time, the concentration in the vapor space will no longer increase. Therefore, this steady state concentration is taken as the maximum aerosol concentration that can be achieved.

The maximum vapor space aerosol concentration for the 1.2 mg/s formation rate was calculated to be about 43 mg/m³. This is less than 0.1% of the lower flammability limit for NPH (about 48 g/m³). For the .12 mg/s and the 12 mg/s formation rates, the maximum concentrations were 8.2 mg/m³ and 220 mg/m³, respectively. The concentration at the higher source rate is less than 0.5% of the LFL.

The effect of two of the assumptions that were made in determining the aerosol formation rate can be examined in relationship to the maximum aerosol concentrations calculated for these three cases. If condensation on the tank dome and walls is neglected, then the total aerosol formation rate is the one calculated from the evaporation from the pool, 13.9 mg/s (0.11 lb_m/hr). This is only slightly higher than the upper bound of the three cases calculated, so the maximum expected concentration of aerosols in the vapor space is expected to be comparable to that case.

Another assumption was that the composition of the liquid from which the aerosols form is the 73 weight percent TBP/27 weight percent NPH reported by Prentice. If it were assumed that the liquid is 35.5 weight percent TBP and 64.5 weight percent NPH, the composition of the original process liquid, the calculated aerosol source term (allowing for condensation on dome and walls) would be 8.6 mg/s. This value is also bounded by the cases calculated. Therefore, even considering large uncertainty in the calculations of the aerosol formation rate, the contribution of liquid organic aerosols to flammability of the vapor space in Tank 103-C is comparatively minor.

Table D-3. C-1 MAEROS Code Input File.

```

1 - NUMBER OF CASES
TANK C-103 VAPOR SPACE MODEL, RELEASE INTO VAPOR SPACE, NO CONDENSATION
SECTIONS  COMPONENTS  NUMBER-OUTPUTS  NUMBER-SOURCES  STATUS
16          1          20          2          0
CONDENSE TP-TABLE NEWCOEF STORE AUTO-BOUNDARIES INITIAL SOURCES
0          2          2          0          1          1          1
PLOTS PLOT-COMPONENTS ROWS COLUMNS MIN-CONC. MAX-CONC.
1          0          20          50          0.          1.
CEILING/V FLOOR/V WALL/V CHI DIFFUSION-THICK DENSITY
.19        .16        .11        1.          1.E-3        906.
LEAK-RATE GAMMA STICK TGRAD-C TGRAD-F TGRAD-W THERMAL COND. G/P
0.          1.          1.          0.          0.          0.          .18
RHO-C RHO-F RHO-W VFRAC-C VFRAC-F VFRAC-W VGRAD-C VGRAD-F VGRAD-W
1.E3 1.E3 1.E3 0.          0.          0.          0.          0.          0.
TURBDS VOLUME MOLECULAR-WT ROUND-OFF REL-ERROR INITIAL STEAM CONC.
.001 2560. 28.8 1.E-6 0.003 0.
TGAS1 TGAS2 PGAS1 PGAS2
317. 400. 101325. 2.E5
SMALLEST-DIAMETER LARGEST-DIAMETER
1.0E-7 1.E-5
INITIAL-MASS-CONC.(KG/M**3) MEAN-DIAMETER GEO-STAND.-DEV.
0. 1.3E-7 2.0
TIME VAPOR-SOURCE-RATE (KG/S)/ AEROSOL SOURCE RATE (LOG-NORMAL)(KG/S)
0. 0.
1.21E-6 1.3E-7 2.0
TIME VAPOR-SOURCE-RATE (KG/S)/ AEROSOL SOURCE RATE (LOG-NORMAL)(KG/S)
1.6E6 0.
1.21E-6 1.3E-7 2.0
OUTPUT TIMES (SECONDS)
5.E1 1.E2 2.E2 4.E2 8.E2 1.6E3 3.2E3 6.4E3 9.6E3 1.3E4 1.9E4 2.6E4 3.8E4 5.1E4
7.7E4 1.0E5 2.0E5 4.0E5 8.0E5 1.6E6
TIME TEMPERATURE (K) PRESSURE (PA)
0. 317. 101325.
1.6E6 317. 101325.

```

Table D-4. MAEROS Code Output for 1.2 mg/s Source Rate. (7 pages)

TANK C-103 VAPOR SPACE MODEL, RELEASE INTO VAPOR SPACE, NO CONDENSATION
THIS IS CASE NUMBER 1 OUT OF 1

NUMBER OF SECTIONS (5-40) = 16
 NUMBER OF CHEMICAL COMPONENTS (1-8) = 1
 NUMBER OF PRINT OUT TIMES (1-20) = 20
 NUMBER OF TIMES IN SOURCE TABLE (2-10) = 2
 STATUS REPORT FLAG (0=NONE/1=SOME/2=A LOT) = 0

 CONDENSATION FLAG (0=NO,1=YES,2=YES CONSTANT VAPOR CONC.) = 0
 NUMBER OF TIMES IN TEMPERATURE AND PRESSURE TABLE (2-20) = 2
 NEW COEFFICIENTS TO BE CALCULATED = 2
 (POSITIVE=CALCULATE/NEGATIVE=USE EXISTING COEFFICIENTS)
 0=READ COEFFICIENTS FROM FILE MAEROS2.COF
 1=AT TGAS1,TGAS2,PGAS1,PGAS2
 2=AT PGAS1,TGAS1
 3=AT PGAS1,TGAS1 AND TGAS2
 4=AT TGAS1,PGAS1 AND PGAS2
 5=SAME AS 1 EXCEPT ONLY DEPOSITION
 6=SAME AS 1 EXCEPT ONLY CONDENSATION
 7=SAME AS 1 EXCEPT ONLY DEPOSITION AND CONDENSATION
 8=SAME AS 2 EXCEPT ONLY CONDENSATION
 STORE SECTIONAL COEFFICIENTS IN MAEROS2.COF (0=NO/1=YES) = 0
 SECTION BOUNDARIES (1=AUTOMATIC/0=USER SPECIFIED) = 1
 INITIAL DISTRIBUTION (1=LOG-NORMAL/0=USER SPECIFIED) = 1
 SOURCE DISTRIBUTION (1=LOG-NORMAL/0=USER SPECIFIED) = 1

 PRINTER PLOT SCALING (NEGATIVE=LOG/POSITIVE=LINEAR) = 1
 (3=USER,2=USER WITH OVERRIDE,1=AUTOMATIC,0=NO PLOTS)
 PLOT INDIVIDUAL COMPONENTS IN ADDITION TO TOTALS (0=NO/1=YES) = 0
 NUMBER OF ROWS FOR PLOTTING (50 MAXIMUM) = 20
 NUMBER OF COLUMNS FOR PLOTTING (101 MAXIMUM) = 50
 MINIMUM CONCENTRATION PLOTTED (FOR ABS. VALUE OF SCALING OF 3) = 0.0000E+00 KG/M**3
 MAXIMUM CONCENTRATION PLOTTED (FOR ABS. VALUE OF SCALING OF 3) = 1.0000E+00 KG/M**3

 AREA OF CEILING OVER CHAMBER VOLUME = 1.9000E-01 1/METER
 AREA OF FLOOR OVER CHAMBER VOLUME = 1.6000E-01 1/METER
 AREA OF WALLS OVER CHAMBER VOLUME = 1.1000E-01 1/METER
 DYNAMIC SHAPE FACTOR = 1.0000E+00
 DIFFUSION BOUNDARY LAYER THICKNESS = 1.0000E-03 METERS
 PARTICLE MATERIAL DENSITY = 9.0600E+02 KG/M**3

 LEAKAGE RATE = 0.0000E+00 M**3/SEC
 AGGLOMERATION SHAPE FACTOR = 1.0000E+00
 AGGLOMERATION STICKING FACTOR (0-1) = 1.0000E+00
 THERMAL GRADIENT FROM CEILING = 0.0000E+00 DEG K/METER
 THERMAL GRADIENT FROM FLOOR = 0.0000E+00 DEG K/METER
 THERMAL GRADIENT FROM WALLS = 0.0000E+00 DEG K/METER

D-13

WHC-SD-WM-SARR-001, REV. 0

Table D-4. MAEROS Code Output for 1.2 mg/s Source Rate. (7 pages)

THERMAL CONDUCTIVITY OF GAS/PARTICLE = 1.8000E-01
 WATER VAPOR MATERIAL DENSITY NEAR CEILING = 1.0000E+03 KG/M**3
 WATER VAPOR MATERIAL DENSITY NEAR FLOOR = 1.0000E+03 KG/M**3
 WATER VAPOR MATERIAL DENSITY NEAR WALL = 1.0000E+03 KG/M**3
 WATER VAPOR MOLE FRACTION NEAR CEILING = 0.0000E+00
 WATER VAPOR MOLE FRACTION NEAR FLOOR = 0.0000E+00
 WATER VAPOR MOLE FRACTION NEAR WALL = 0.0000E+00
 WATER VAPOR GRADIENT NEAR CEILING = 0.0000E+00 KG-MOLE/M**4
 WATER VAPOR GRADIENT NEAR FLOOR = 0.0000E+00 KG-MOLE/M**4
 WATER VAPOR GRADIENT NEAR WALL = 0.0000E+00 KG-MOLE/M**4
 TURBULENT DISSIPATION RATE = 1.0000E-03 M**2/SEC**3
 CHAMBER VOLUME = 2.5600E+03 M**3
 MOLECULAR WEIGHT OF SUSPENDING GAS = 2.8800E+01 KG/KG-MOLE
 MACHINE UNIT ROUND OFF ERROR = 1.0000E-06
 RELATIVE ERROR TOLERANCE = 3.0000E-03
 INITIAL CONDENSIBLE VAPOR CONCENTRATION = 0.0000E+00 KG/M**3
 FIRST GAS TEMPERATURE (TGAS1) = 3.1700E+02 DEG K
 SECOND GAS TEMPERATURE (TGAS2) = 4.0000E+02 DEG K
 FIRST GAS PRESSURE (PGAS1) = 1.0133E+05 N/M**2
 SECOND GAS PRESSURE (PGAS2) = 2.0000E+05 N/M**2

SMALLEST PARTICLE DIAMETER = 1.0000E-07 M
 LARGEST PARTICLE DIAMETER = 1.0000E-05 M
 USING THE ABOVE RANGE THE SECTION BOUNDARIES ARE:

SECTION	DIAMETER RANGE (METERS)
1	1.0000E-07 -- 1.3335E-07
2	1.3335E-07 -- 1.7783E-07
3	1.7783E-07 -- 2.3714E-07
4	2.3714E-07 -- 3.1623E-07
5	3.1623E-07 -- 4.2170E-07
6	4.2170E-07 -- 5.6234E-07
7	5.6234E-07 -- 7.4989E-07
8	7.4989E-07 -- 1.0000E-06
9	1.0000E-06 -- 1.3335E-06
10	1.3335E-06 -- 1.7783E-06
11	1.7783E-06 -- 2.3714E-06
12	2.3714E-06 -- 3.1623E-06
13	3.1623E-06 -- 4.2170E-06
14	4.2170E-06 -- 5.6234E-06
15	5.6234E-06 -- 7.4989E-06
16	7.4989E-06 -- 1.0000E-05

LOG-NORMAL INITIAL DISTRIBUTION
 COMPONENT KG/M**3 MEAN DIAMETER (M) STD. DEV.

Table D-4. MAEROS Code Output for 1.2 mg/s Source Rate. (7 pages)

1	0.0000E+00	1.3000E-07	2.0000E+00
SECTION INITIAL COMPONENT CONCENTRATION (KG/M**3)			
1	0.0000E+00		
2	0.0000E+00		
3	0.0000E+00		
4	0.0000E+00		
5	0.0000E+00		
6	0.0000E+00		
7	0.0000E+00		
8	0.0000E+00		
9	0.0000E+00		
10	0.0000E+00		
11	0.0000E+00		
12	0.0000E+00		
13	0.0000E+00		
14	0.0000E+00		
15	0.0000E+00		
16	0.0000E+00		

Table D-4. MAEROS Code Output for 1.2 mg/s Source Rate. (7 pages)

SOURCE RATES FOR CONDENSIBLE VAPOR AND AEROSOL						
NUMBER	TIME (S)	VAPOR (KG/S)	COMPONENT	MASS RATE (KG/S)	MEAN DIAMETER (M)	GEOMETRIC STD. DEV.
1	0.0000E+00	0.0000E+00	1	1.2100E-06	1.3000E-07	2.0000E+00
2	1.6000E+06	0.0000E+00	1	1.2100E-06	1.3000E-07	2.0000E+00

BASED ON THE ABOVE LOG-NORMAL PARAMETERS THE SECTIONAL SOURCE RATES ARE:

TIME FOR THE FOLLOWING SOURCE RATE = 0.0000E+00 SEC

SECTION COMPONENT SOURCE RATES (KG/SEC)

1	3.0290E-07
2	2.9846E-07
3	2.4805E-07
4	1.7393E-07
5	1.0289E-07
6	5.1354E-08
7	2.1623E-08
8	7.6804E-09
9	2.3010E-09
10	5.8151E-10
11	1.2409E-10
12	2.2389E-11
13	3.4531E-12
14	4.4556E-13
15	5.5695E-14
16	0.0000E+00

TIME FOR THE FOLLOWING SOURCE RATE = 1.6000E+06 SEC

SECTION COMPONENT SOURCE RATES (KG/SEC)

1	3.0290E-07
2	2.9846E-07
3	2.4805E-07
4	1.7393E-07
5	1.0289E-07
6	5.1354E-08
7	2.1623E-08
8	7.6804E-09
9	2.3010E-09
10	5.8151E-10
11	1.2409E-10
12	2.2389E-11
13	3.4531E-12
14	4.4556E-13
15	5.5695E-14
16	0.0000E+00

NUMBER OUTPUT TIMES

Table D-4. MAEROS Code Output for 1.2 mg/s Source Rate. (7 pages)

	SECONDS	HOURS
1	5.0000E+01 =	1.3889E-02
2	1.0000E+02 =	2.7778E-02
3	2.0000E+02 =	5.5556E-02
4	4.0000E+02 =	1.1111E-01
5	8.0000E+02 =	2.2222E-01
6	1.6000E+03 =	4.4444E-01
7	3.2000E+03 =	8.8889E-01
8	6.4000E+03 =	1.7778E+00
9	9.6000E+03 =	2.6667E+00
10	1.3000E+04 =	3.6111E+00
11	1.9000E+04 =	5.2778E+00
12	2.6000E+04 =	7.2222E+00
13	3.8000E+04 =	1.0556E+01
14	5.1000E+04 =	1.4167E+01
15	7.7000E+04 =	2.1389E+01
16	1.0000E+05 =	2.7778E+01
17	2.0000E+05 =	5.5556E+01
18	4.0000E+05 =	1.1111E+02
19	8.0000E+05 =	2.2222E+02
20	1.6000E+06 =	4.4444E+02

TIME (SEC)	GAS TEMPERATURE (DEG K)	GAS PRESSURE (N/M**2)
0.0000E+00	3.1700E+02	1.0133E+05
1.6000E+06	3.1700E+02	1.0133E+05

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Table D-4. MAEROS Code Output for 1.2 mg/s Source Rate. (7 pages)

TANK C-103 VAPOR SPACE MODEL, RELEASE INTO VAPOR SPACE, NO CONDENSATION
 TIME = 0.0000E+00 SECONDS = 0.0000E+00 HOURS
 TEMPERATURE = 3.1700E+02 DEG K PRESSURE = 1.0133E+05 N/M**2

SECTION	DIAMETER RANGE (M)		KG/M**3	NUMBER/M**3	KG
1	1.0000E-07	-- 1.3335E-07	0.0000E+00	0.0000E+00	0.0000E+00
2	1.3335E-07	-- 1.7783E-07	0.0000E+00	0.0000E+00	0.0000E+00
3	1.7783E-07	-- 2.3714E-07	0.0000E+00	0.0000E+00	0.0000E+00
4	2.3714E-07	-- 3.1623E-07	0.0000E+00	0.0000E+00	0.0000E+00
5	3.1623E-07	-- 4.2170E-07	0.0000E+00	0.0000E+00	0.0000E+00
6	4.2170E-07	-- 5.6234E-07	0.0000E+00	0.0000E+00	0.0000E+00
7	5.6234E-07	-- 7.4989E-07	0.0000E+00	0.0000E+00	0.0000E+00
8	7.4989E-07	-- 1.0000E-06	0.0000E+00	0.0000E+00	0.0000E+00
9	1.0000E-06	-- 1.3335E-06	0.0000E+00	0.0000E+00	0.0000E+00
10	1.3335E-06	-- 1.7783E-06	0.0000E+00	0.0000E+00	0.0000E+00
11	1.7783E-06	-- 2.3714E-06	0.0000E+00	0.0000E+00	0.0000E+00
12	2.3714E-06	-- 3.1623E-06	0.0000E+00	0.0000E+00	0.0000E+00
13	3.1623E-06	-- 4.2170E-06	0.0000E+00	0.0000E+00	0.0000E+00
14	4.2170E-06	-- 5.6234E-06	0.0000E+00	0.0000E+00	0.0000E+00
15	5.6234E-06	-- 7.4989E-06	0.0000E+00	0.0000E+00	0.0000E+00
16	7.4989E-06	-- 1.0000E-05	0.0000E+00	0.0000E+00	0.0000E+00
TOTAL			0.0000E+00	0.0000E+00	0.0000E+00

Table D-4. MAEROS Code Output for 1.2 mg/s Source Rate. (7 pages)

TANK C-103 VAPOR SPACE MODEL, RELEASE INTO VAPOR SPACE, NO CONDENSATION
 TIME = 8.0000E+05 SECONDS = 2.2222E+02 HOURS
 TEMPERATURE = 3.1700E+02 DEG K PRESSURE = 1.0133E+05 N/M**2

SECTION	DIAMETER RANGE (M)	KG/M**3	NUMBER/M**3	KG
1	1.0000E-07 -- 1.3335E-07	1.1119E-07	1.5697E+11	2.8463E-04
2	1.3335E-07 -- 1.7783E-07	2.1392E-07	1.2736E+11	5.4764E-04
3	1.7783E-07 -- 2.3714E-07	3.9068E-07	9.8086E+10	1.0002E-03
4	2.3714E-07 -- 3.1623E-07	6.6519E-07	7.0425E+10	1.7029E-03
5	3.1623E-07 -- 4.2170E-07	1.0880E-06	4.8573E+10	2.7852E-03
6	4.2170E-07 -- 5.6234E-07	1.7625E-06	3.3183E+10	4.5121E-03
7	5.6234E-07 -- 7.4989E-07	2.9851E-06	2.3064E+10	7.4370E-03
8	7.4989E-07 -- 1.0000E-06	4.9193E-06	1.6470E+10	1.2593E-02
9	1.0000E-06 -- 1.3335E-06	8.2052E-06	1.1584E+10	2.1005E-02
10	1.3335E-06 -- 1.7783E-06	1.1233E-05	6.6880E+09	2.8758E-02
11	1.7783E-06 -- 2.3714E-06	8.6183E-06	2.1617E+09	2.2042E-02
12	2.3714E-06 -- 3.1623E-06	2.5841E-06	2.7359E+08	6.6154E-03
13	3.1623E-06 -- 4.2170E-06	2.6970E-07	1.2041E+07	6.9042E-04
14	4.2170E-06 -- 5.6234E-06	1.0002E-08	1.8830E+05	2.5604E-05
15	5.6234E-06 -- 7.4989E-06	1.3900E-10	1.1036E+03	3.5585E-07
16	7.4989E-06 -- 1.0000E-05	7.6535E-13	2.5624E+00	1.9593E-09
TOTAL		4.2960E-05	5.9486E+11	1.1000E-01

TOTAL AEROSOLIZED MASS REMOVED SINCE LAST OUTPUT = 4.8399E-01 KG
 CUMULATIVE OVER ALL TIME = 8.5800E-01 KG

TOTAL SINCE LAST OUTPUT TIME

CEILING (KG)	0.0000E+00
WALLS (KG)	1.5741E-04
FLOOR (KG)	4.8384E-01
LEAKED (KG)	0.0000E+00
TOTAL (KG)	4.8399E-01
CUMULATIVE (KG)	8.5800E-01

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APPENDIX E
VEHICLE-FUEL RELEASE LEADING TO BURN IN TANK C-103
PROBABILISTIC ANALYSIS

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Westinghouse
Hanford Company

Internal
Memo

From: Risk Assessment Technology 29220-93-0038
Phone: 6-1083 H4-65
Date: March 9, 1994
Subject: LETTER REPORT

To: R. L. Guthrie H4-61
cc: M. V. Shultz H4-65
M. D. Zentner H4-65
File/LB

Attached is the letter report "Vehicle-Fuel Release Leading to Burn in Tank C-103 Probabilistic Analysis" prepared by M. V. Shultz and myself.

Mike F. Reardon

Mike F. Reardon
Engineer

s1

Attachment

APPENDIX E

**VEHICLE-FUEL RELEASE LEADING TO BURN IN TANK C-103
PROBABILISTIC ANALYSIS**

E.1 INTRODUCTION

Two incidents in the last two years have raised a concern about motor vehicles that enter the tank farms. There is a possibility that an accident can occur that results in the fuel carried by the vehicle entering a waste storage tank and possibly igniting. The analysis documented in this report was performed to evaluate this accident at single-shell tank C-103. The analysis used event tree logic to obtain an estimate of the annual frequency of a pool fire or ignition of gasoline vapors in tank C-103. The estimate of annual frequency contains conservatism in the initiating event frequency as well as the various event probabilities of the event tree.

E.2 SUMMARY AND CONCLUSIONS

The results of the analysis show that accidents with undesirable results have a frequency that is considered credible; that is, greater than $1.0E-06$ per year. The uncertainty in some of the values used in the event tree analysis necessitated application of conservative values. No compelling evidence was found that indicated less conservative values should be used. The results of the event tree show that the frequency of burning fuel entering a riser and starting an organic pool fire in tank 103-C is $6.71E-05$ per year. The probability of gasoline leaking into a riser leading to an LFL condition and eventual ignition is $6.64E-06$ per year. Since the calculated frequency of undesirable consequence end states is not less than $1.0E-06$, some protective measures, either administrative or physical, may be necessary.

E.3 DISCUSSION

Two possible scenarios were considered in assessing the safety of tank C-103 with respect to gasoline spills from vehicles. The first scenario accounted for a leak of gasoline from a vehicle due to an accident that results in the puncture of the fuel tank by an object at grade level at C-103. Generally, this accident would be initiated by a vehicle driver backing over an object such as a riser or instruments. The gasoline leaking from the vehicle's fuel tank would then ignite due to a source of sparks from the accident or contact with hot elements of the vehicle's engine or exhaust system. Finally, the burning fuel would enter the tank through cracks in the cover blocks above the pump pit or through a riser damaged in the accident. The second scenario accounted for a leak from a vehicle similar to that described above, except that the leaking fuel does not immediately ignite but still enters the tank. The gasoline vapor in the waste tank then builds to the lower flammability point and is ignited by an ignition source in the tank. This ignition results in a rapid burn or deflagration.

Two potential routes of entry were identified. The first is through the cracks in cover blocks over the pump pit allowing fuel into the tank through the pit drain. This route could only be possible if the truck could get onto the cover blocks over the pump pit. The other route of entry to the tank would be through a tank riser damaged by the vehicle during the accident which is open to receive leaking fuel. Inspection of the C-103 site showed that the entry route through the cover blocks of the pit structure was not credible since the structure rises 2 to 3 feet above grade. A vehicle would have great difficulty getting onto the cover. The second route of entry through a damaged riser is considered feasible. It forms the basis of the scenario evaluated in the event tree developed in this analysis.

The event tree that follows shows a number of events that, depending upon which combinations occur, can result in different consequences. Each event is a decision point; either the event did happen (the lower branch of an event) or it did not (the upper branch of an event). When these decisions are traced along the branches of an event tree, they result in different endstates or consequences. In the event tree, the events or decision points are shown along the top of the figure, while the endstates and the sequence frequencies are shown on the right edge of the figure. A discussion of these events and the assumptions supporting the assigned probabilities follows.

VEHICLES EXPERIENCE FUEL TANK RUPTURE IN TANK FARM

This event is the initiator and has the units of events per year per tank. It represents current Hanford historical data specifically related to "dry well vans" that have experienced fuel tank ruptures. These vehicles enter the tank farms on a regular but unspecified frequency. The following assumptions are made to calculate the initiating event frequency:

1. The number of risers that protrude to a height sufficient to interfere with a motor vehicle fuel tank are the same for each of the 149 single shell tanks
2. The number of risers for each single shell tank are the same
3. The riser placement and tank location within any single shell tank farm will necessitate similar backing actions to place a vehicle in the proper location for work to be performed
4. No changes occur in either the number of vehicle entries or riser configurations in the future beyond current conditions

The initiating event value is the result of dividing the number of tanks (149) in farms where "dry well vans" are used into the number of accidents that result per year. This is analogous to considering the tanks in the farms as an "area" within which a random event of characteristic frequency could take place. One such event took place in each of the past two years.

The accident frequency used in this analysis is $6.71E-03$ accidents per tank-year. In the past two years, there have been two accidents in the tank farms in which a vehicle has backed over a riser and punctured its fuel tank. The accidents are described in Unusual Occurrence Reports (UORs) and summarized below.

- UOR 1992-0029 - In this event a drywell monitoring van backed over a riser at 104-SX and punctured its gas tank. Two gallons of gas spilled onto the ground and five more were caught in a bucket while spilling. It is important to note that the driver did a 360 walk-around prior to backing up and noticed the riser, but still hit the riser anyway. The riser was not opened in the accident.
- UOR 1993-0076 - In this event, a drywell monitoring vehicle backed into a riser at 108-S. A pinhole leak in the vehicle's gas tank resulted, but the riser was not opened in the accident.

A review of UORs shows three events of a nature similar to those of concern in this analysis. In April 1992 there was a backing accident at the Grand Junction, Colorado site that resulted in the spill of approximately 25 gallons of gasoline (ALO-GEO-GJO-1992-004). In November 1992, the Los Alamos National Laboratory experienced a backing accident that resulted in the spill of 20 gallons of gasoline (ALO-LA-LANL-SECURITY-1992-0010). In February 1994, at the Sandia National Laboratory, there was a backing accident that very closely approximated the accident being depicted in this analysis (ALO-KO-SNL-NMSEC-1994-0002). A vehicle backed into a metal post (approximately two feet high) that punctured the gas tank. The vehicle was stuck on the post and the gasoline leaked into a water control valve pit until the tank was empty. Approximately 10 to 15 gallons of gasoline were involved. The only thing lacking in the accident that is modeled in this analysis was ignition of the gasoline.

RISER IS BROKEN OPEN OR OFF BY ACCIDENT

The risers are made of low carbon steel and are not prone to brittle fracture, especially with the low energy forces involved in a simple "fender-bender," but a 1991-1992 UOR shows that tank farm risers can corrode and as a result break easily upon impact. This UOR records that a thermocouple riser was broken off when a front-end loader backed over it at T Farm. Inspection of the riser revealed that it was heavily corroded and may not have required the mass of a front-end loader to shear it off. For these reasons, the probability of this event is conservatively taken as 1.0 for this analysis.

LEAKING GASOLINE ENTERS TANK THROUGH RISER

This event accounts for the gasoline from the punctured gas tank entering the open riser and flowing into the tank. This event is also given a probability of 1.0 for conservation. Because the puncture point in the fuel tank is the place of impact between the riser and the vehicle the hole will be above the damaged riser allowing gasoline to flow into the riser.

LEAKING GASOLINE IS IGNITED

This event accounts for the chance that the gasoline will ignite, given that it has already spilled from a ruptured fuel tank. The value was taken from WHC-SD-TP-RPT-007, Revision 0, a Westinghouse Hanford transportation safety analysis which quoted vehicle fires in a non-rollover accident as 1.0E-02.

GASOLINE VAPORIZES TO >LFL IN DOME SPACE

This event describes the situation in which the gasoline has leaked into the tank, but did not ignite immediately. This event is also conservatively taken as 1.0 under the assumption that if any gas leaks into the tank at all, enough gasoline can leak into the tank to set up an LFL (lower flammability limit) condition.

DOMESTIC SPACE IGNITION SOURCE RESULTS IN IGNITION OF GASOLINE VAPORS

This situation is considered to be similar to the ignition hazard at the hydrogen-generating tank-101-SY. The probability of an ignition source present in 101-SY is 1.0E-03 as stated in LAUR-02-3196, Revision 5, Section 5-8 (Safety Assessment for Proposed Pump Operation to Mitigate Episodic Gas Releases in Tank 241-SY-101). Although the system configuration differs greatly between 101-SY and C-103, this data application is considered conservative as 101-SY has more spark generating components such as cameras, lights and other instruments.

BURNING GASOLINE IS SUFFICIENT TO INITIATE POOL FIRE

This event is given a probability of 1.0 as any burning liquid entering the tank is considered sufficient to start the organic layer burning. The event is included only to better illustrate the processes leading to the endstates.

E.4 RESULTS

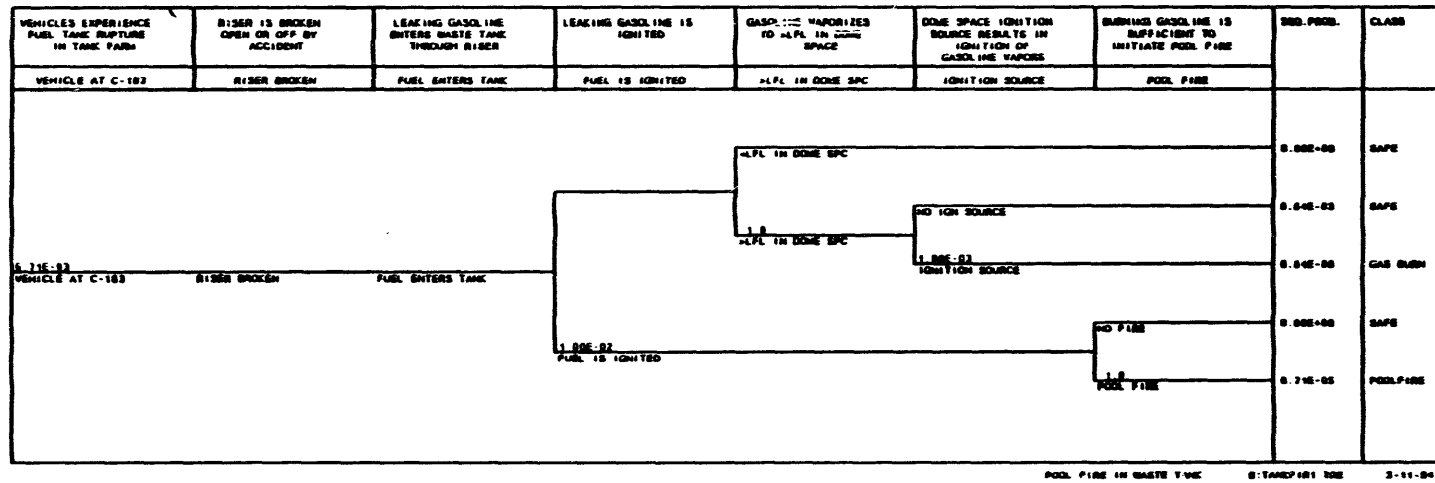
Accident sequences were evaluated in the event tree shown in Figure 1. The frequency for a pool fire in the C-103 tank was calculated to be $6.71\text{E-}05$ per year. The frequency for vapor ignition in the tank was calculated to be $6.64\text{E-}06$ per year. The frequency of pool fire is driven by the likelihood of ignition of leaking fuel. The frequency of a vapor ignition event is driven by the likelihood of an ignition source being present in the tank. Since neither frequency is less than $1.0\text{E-}06$ per year, these sequences cannot be considered incredible.

E.5 REFERENCES

Edwards, J. N., *Safety Assessment for Proposed Pump Operation to Mitigate Episodic gas Releases in Tank 241-C-101*, Los Alamos National Laboratory, Los Alamos, New Mexico.

Kelly, J. e. and M. d. Zentner, December 1993, *Standard Transportation Risk Assessment Methodology*, Westinghouse Hanford Company, Richland, Washington.

Figure E-1. Event Tree for Vehicle Accident Caused Fuel Leak Fires in the C-103 Waste Tank.



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APPENDIX F

**TEMPERATURE DIFFERENCE IN HEADSPACE AIR
CAUSED BY DECAY HEAT DISSIPATION**

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APPENDIX F

TEMPERATURE GRADIENTS IN HEADSPACE AIR
CAUSED BY DECAY HEAT DISSIPATION

The transfer of decay heat energy upward from the waste surface, through headspace air imposes a temperature difference across headspace air. The magnitude of the temperature gradient plays a role in the formation of condensation aerosols as described in Appendix D and in Section 6.1.3 of the main body of this report. Also, it is important to know passive heat dissipation capabilities under dry conditions (i e. where evaporation and condensation do not contribute significantly to heat transfer). For these reasons the magnitude of the temperature drop across headspace air is computed in this appendix.

Three different heat transport mechanisms for transferring decay heat from the upper surface of the waste to the inner surface of the concrete dome can be identified:

- Radiation
- Convection
- evaporation/condensation.

The last of these, evaporation/condensation could be important for tanks in which aqueous supernatant liquid covers the waste. However, for waste which exposed a dry upper surface to headspace air, evaporation/condensation would be relatively unimportant. Tank C-103 has a floating organic liquid layer that could suppress the rate of water evaporation. Evaporation and condensation of water vapor is neglected in the analysis that follows. Predicted temperature differences will therefore be larger than would be calculated if evaporation were accounted for. Higher temperature differences lead to higher predicted aerosol concentrations (see Appendix D); hence this assumption is conservative with respect to predicted organic aerosol concentrations.

Heat transport to the concrete dome caused by the reflux of organic liquid can be estimated from vapor condensation rates computed in Appendix D. Based on a condensation flux of 2.26×10^{-5} lb/hr ft², an area of 4418 ft², and a latent heat of 110 BTU/lb (Hougen et al. 1954), the heat transfer rate is:

$$Q = 2.26 \times 10^{-5} \frac{\text{lb}}{\text{hr ft}^2} \times 4418 \text{ ft}^2 \times 110 \frac{\text{BTU}}{\text{lb}} = 11 \frac{\text{BTU}}{\text{hr}}$$

This heat transfer rate is small (<0.1%) compared to the total, and evaporation/condensation of organic liquid can be neglected as a significant heat transport mechanism.

NATURAL CONVECTION

Natural convection was quantified on the basis of heat transfer correlations (McAdams 1954) that relate Nusselt no. to the product Grashov and Prandtl numbers:

$$N = a [X]^n \quad (F-1)$$

where:

- Nu = Nusselt number = hL/k
- h = Heat transfer coefficient
- L = Characteristic length
- k = Thermal conductivity of fluid
- a = A constant
- X = Gr.Pr
- Gr = Grashov number =

$$\frac{L^3 \rho^2 \beta \Delta T}{\mu^2}$$

- ρ = Fluid density
- β = Fluid thermal expansion coefficient
- ΔT = Temperature difference in fluid
- μ = Viscosity of fluid
- Pr = Prandtl number = $C_p \mu/k$
- C_p = Heat capacity of fluid,
- n = A constant.

Numerical values of constants a and n depend on the value of X and the physical configuration that applies.

For tank C-103, L is 75 ft, the tank diameter. The value of X for L = 75 ft, for $\Delta T = 1$ °F, and for fluid properties evaluated for air at 105 °F X was computed to be 7×10^{12} . This value is in the turbulent range, for which the value of n in Equation (F-1) has a value of 1/3 (McAdams 1954). For horizontal enclosed spaces heated from below, a simplified form of Equation (F-1) is derivable from the work of McAdams (1954) to be:

$$h_c = 0.1 \Delta T^{1/3} \quad (F-2)$$

where:

$$h_c = \text{BTU/hr}^\circ\text{F ft}^2$$

$$\Delta T = \text{Temperature difference, } ^\circ\text{F.}$$

The constant, 0.1, in Equation (F-2) applies for air at 1 atm. pressure and ordinary temperatures.

RADIATION HEAT TRANSFER

Radiation of heat from the waste surface to the tank dome was quantified on the basis of the following simplifying assumptions and numerical estimates.

- Geometry is representable by two discs (75 ft dia.) separated by a nonabsorbing medium, connected with cylindrical walls that are nonconducting and reradiating.
- Distance between discs is 18.5 ft, the estimated distance between the current waste surface and the top of the cylindrical wall of the tank.
- A view factor of 0.77, taken from Figure 4.11 of McAdams (1954) for a diameter/spacing ratio of 75/18.5, applies for the tank.
- Absorption of radiation by water vapor in headspace air and radiation from water vapor to the dome were neglected.
- Emissivities of organic liquid which covers the waste surface, and concrete which makes up the dome, were assigned values of 0.82 and 0.91 respectively on the basis of data presented by McAdams (1954).

Based on the model characterized by the assumptions described above, the radiation flux may be calculated from the following equation (McAdams 1954):

$$q_1 \rightarrow q_2 = A_1 \mathcal{F}_{12} \sigma (T_1^4 - T_2^4) \quad (\text{F-3})$$

where:

- $q_1 \rightarrow q_2$ = Radiation heat transport rate from surface 1 to surface 2
- A_1 = Area of surface 1
- \mathcal{F}_{12} = Radiation factor
- σ = Stefan - Boltzman constant
- T_1, T_2 = Absolute temperatures of surfaces 1 and 2.

The product $A_1 \mathcal{F}_{12}$ for the case of two source-sink zones (A_1 and A_2) with relatively high emissivities is related to controlling parameters by the following equation (McAdams 1954).

$$\frac{1}{A_1 \mathcal{F}_{12}} = \frac{1}{A_1} \left(\frac{1}{\epsilon_1} - 1 \right) + \frac{1}{A_2} \left(\frac{1}{\epsilon_2} - 1 \right) + \frac{1}{A_1 \bar{F}_{12}} \quad (F-4)$$

where:

- ϵ_1 = Emissivity of surface 1
- ϵ_2 = Emissivity of surface 2
- \bar{F}_{12} = View factor.

Substituting applicable values of ϵ_1 , ϵ_2 , and \bar{F} into Equation (E-4) results in a predicted \mathcal{F}_{12} value of 0.62.

SUM OF RADIATION AND CONVECTION

Overall heat transfer rate resulting from radiation and convection was computed by summing Equations (F-3) and (F-2), taking surface area to be that of exposed waste, 4418 ft² and the waste surface temperature to be 106°F. Results are summarized in Table F-1 and shown graphically in Figure F-1.

Table F-1. Heat Transport Rate Computed for Convection and Radiation in Tank C-103.

ΔT^* °F	Heat transport rate - BTU/hr		
	Convection	Radiation	Total
1	442	3,402	3,840
2	1,113	6,759	7,870
3	1,913	10,073	11,990
4	2,805	13,431	16,240
5	3,777	16,744	20,520
6	4,816	20,013	24,830

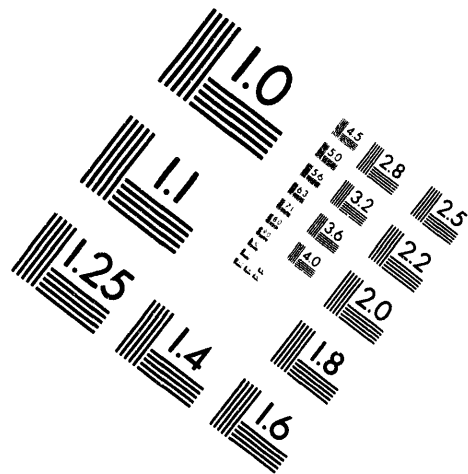
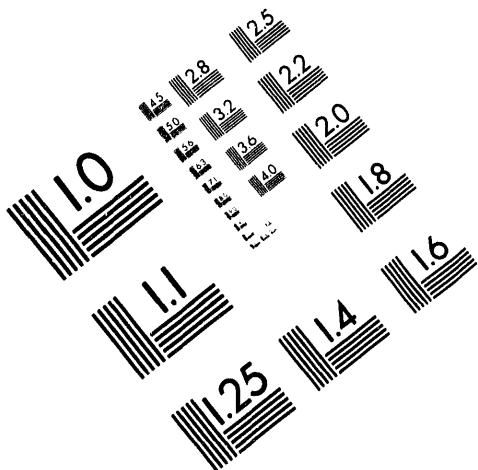
*Temperature of waste surface minus dome surface temperature



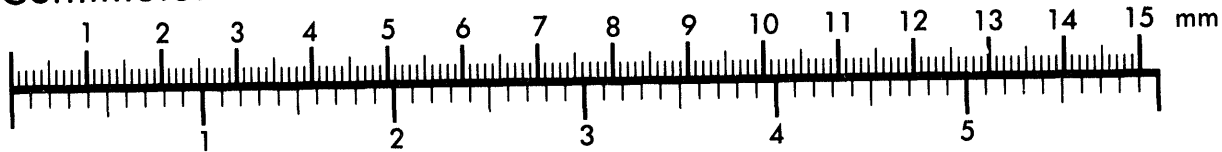
AIM

Association for Information and Image Management

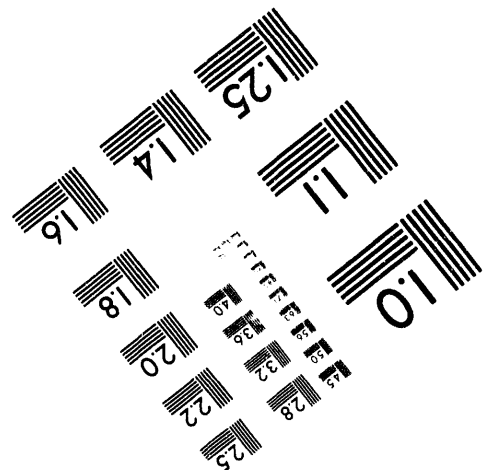
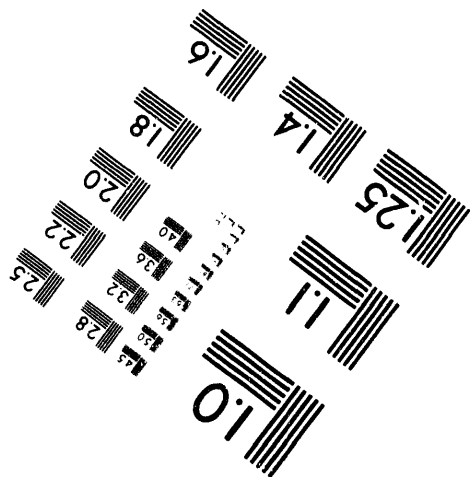
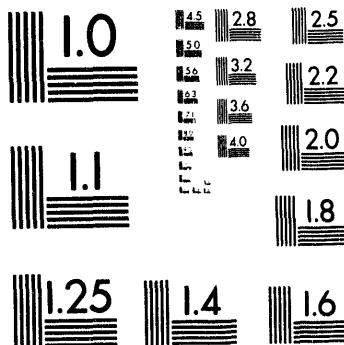
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202



Centimeter



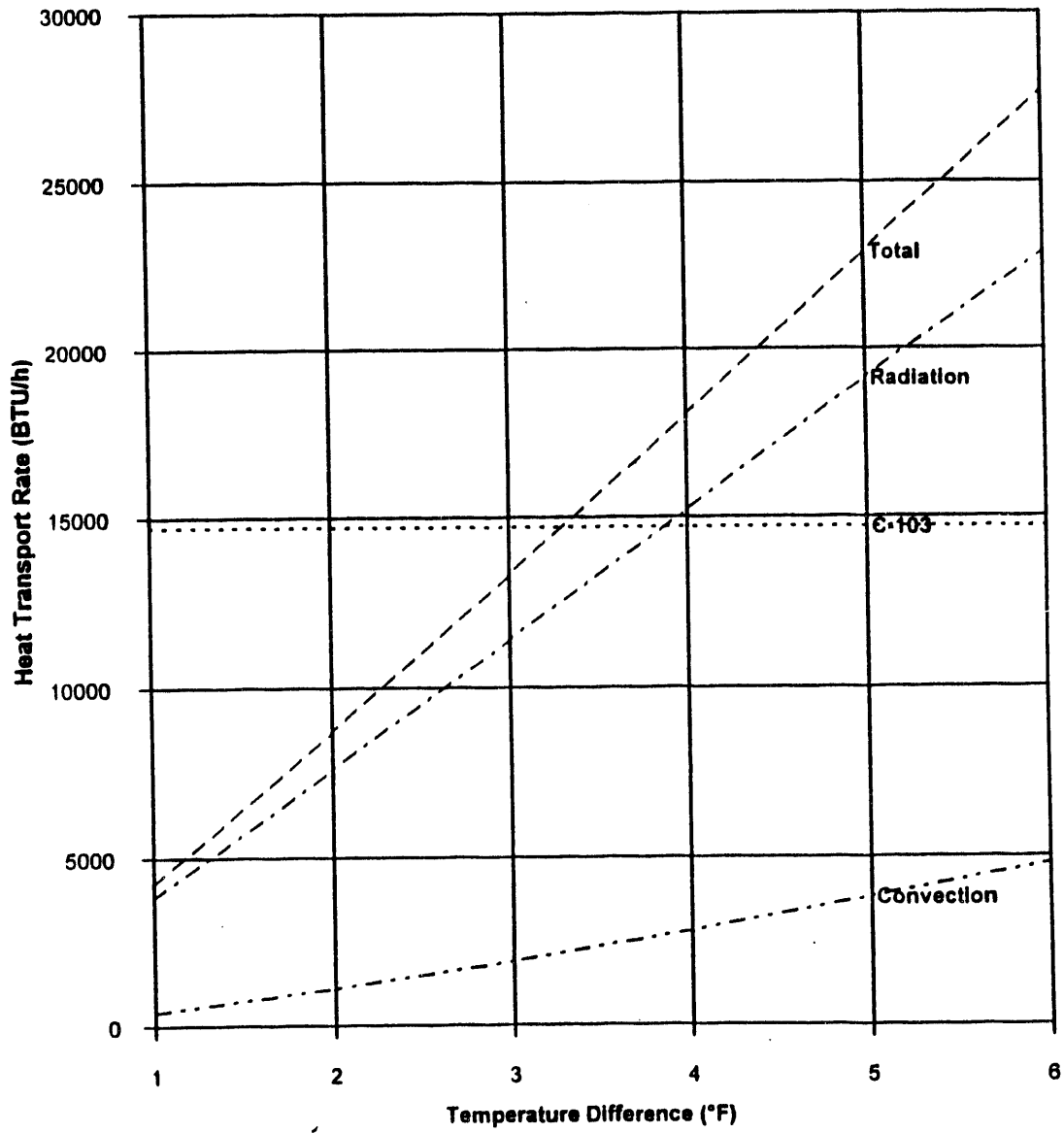
Inches



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Figure F-1.



As indicated by the data of Table F-1, radiation is the dominant heat transport mechanism. The other key feature of the results shown in Table F-1 is that the temperature difference across the headspace air volume is quite small, a few degrees Fahrenheit, for the range of heat loads considered.

This temperature difference is 3.3 °F (1.8 °C) is reflective of the total temperature drop across boundary layers at both the heated and cooled surfaces. The temperature difference across each boundary layer is thus predicted to be less than 2 °F. Two important conclusions that may be drawn from this result are

1. Decay heat can be dissipated from tank C-103 by passive processes that do not depend on the evaporation of water from the surface of the waste
2. Temperature gradients that could lead to the formation of aerosols by condensation are quite small, less than 2 °F across boundary layers at the organic liquid-air interface and at the air-dome surface.

An estimated temperature difference for tank C-103 is identified on Figure F-1 as approximately 3.3 °F. This estimate is based on an estimated heat transfer rate across the organic-air interface. This rate was calculated from the total heat load (18,000 Btu/h) minus the fraction of the heat predicted to be transferred from the bottom of the tank (Crowe et al. 1993):

$$\text{Transfer rate} = 18,000 \frac{\text{BTU}}{\text{h}} \times (1-0.18) = 14,800 \frac{\text{BTU}}{\text{h}}$$

REFERENCES

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.

McAdams, W. H., 1954, "Heat Transmission", McGraw-Hill, New York.

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