

ENGINEERING CHANGE NOTICE

Page 1 of 2

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Proj. ECN

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 Revision is needed to update the technical basis for program developments over the past three years, to segregate the technical basis from DQO requirements, and to state criteria for termination of Standard Hydrogen Monitoring System (SHMS) monitoring or a waste tank.

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Operating Specification	<input type="checkbox"/>	Interface Control Drawing	<input type="checkbox"/>	Spares Multiple Unit Listing	<input type="checkbox"/>
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FSAR/SAR	<input type="checkbox"/>	IEFD Drawing	<input type="checkbox"/>	Process Control Manual/Plan	<input type="checkbox"/>
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21. Approvals

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Cog. Mgr. <i>R. M. Hodges</i>	<u>4/15/98</u>	QA	_____
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# Flammable Gas Tank Safety Program: Technical Basis for Gas Analysis and Monitoring

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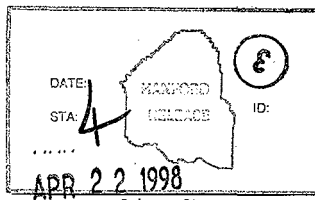
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*Scott D. Estey*  
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## 1.0 INTRODUCTION

### The Flammable Gas Safety Issue

Several Hanford waste tanks have been observed to exhibit periodic releases of significant quantities of flammable gases. Because potential safety issues have been identified with this type of waste behavior, applicable tanks were equipped with instrumentation offering the capability to continuously monitor gases released from them.

This document was written to cover three primary areas: 1) describe the current technical basis for requiring flammable gas monitoring, 2) update the technical basis to include knowledge gained from monitoring the tanks over the last three years, 3) provide the criteria for removal of Standard Hydrogen Monitoring System(s) (SHMS) from a waste tank or termination of other flammable gas monitoring activities in the Hanford Tank farms.

## 2.0 BASIS FOR GAS MONITORING

This section identifies the major issues driving the operation of the flammable gas monitoring systems, the data that each issue requires, and how the data will be used. The flammable gas monitoring systems installed on the tanks are known as SHMS.

### 2.1 SUPPORT OF WORK CONTROLS AND WORKER SAFETY

Gas mixtures generated and released by Hanford waste tanks are not only potentially flammable but may pose toxicological risks. Gas monitoring supports work controls and worker safety by helping to define the risks due to the gas releases from the waste tanks. This is primarily achieved through knowledge of the composition and concentrations of gases in the tank atmosphere. Much of the information obtained by continuous monitoring cannot be obtained by the periodic sampling and analysis methods employed by the tank vapor program or by use of hand-held combustible gas meters.

In addition, the SHMS provides an alarm function in support of work controls and worker safety. The alarm threshold for the SHMS is set at 6,250 ppmv hydrogen. When hydrogen is detected in a tank's atmosphere at this concentration, the tank's atmosphere may have reached a fuel concentration that is approaching 25% of the lower flammable limit (LFL). The detection of this hydrogen concentration by the SHMS triggers immediate actions intended to place the tank in a stable condition until a additional corrective action measures can be determined and implemented.

## 2.2 OBTAIN DATA TO SUPPORT UNREVIEWED SAFETY QUESTION CLOSURE AND SAFETY ISSUE RESOLUTION

The information needed to analyze the flammable gas safety issue is that which can state whether the gas being released is flammable in the tank atmosphere, how often such a condition might occur, and the magnitude of the risk associated with the gas release. Several gases are produced by radiolytic and chemical reactions in Hanford tank waste including hydrogen, nitrous oxide, ammonia, and nitrogen. Gas monitoring is primarily directed to detection of hydrogen in the released gases since it is known that this gas is the primary component that causes the flammability hazard in the waste tanks. All the SHMS are primarily configured to quantify this gas. Two other prevalent gases, nitrogen and nitrous oxide, are known to be produced in significant quantity. Although both gases act as diluents when tank headspace flammability concerns are present, nitrous oxide can function as an oxidizer for in-situ gas mixtures.

Other gases that are known to be released in measurable quantities are ammonia and hydrocarbon gases. Ammonia is of interest because of its toxic properties and because it can contribute to the fuel content of the released gases when it is present at sizeable concentrations. In certain modes of gas release demonstrated by double shell-tanks (DSTs), the concentrations of ammonia can become large enough to be both a toxic and flammability concern. The hydrocarbon gases, methane and total non-methane hydrocarbons (TNMHC), are energetic fuels that also contribute to the fuel loading in a tank's atmosphere. Oxygen is produced, as is hydrogen, from the radiolytic decomposition of water. In typical tank waste conditions, oxygen is scavenged by the waste and is not available to participate in gas phase reactions.

### 2.2.1 Monitor the Transient Behavior of Waste Tanks

With the on-line quantification and, when so equipped, speciation capabilities of the SHMS, important information about a tank's atmosphere and waste behavior can be obtained. The combination of the SHMS on-line analysis capabilities and subsequent off-line analysis of the SHMS data and/or samples provide the information necessary to determine the magnitude, frequency, and composition of the gases released.

Magnitude of Gas Releases - SHMS are capable of providing the samples and the data needed to quantify gas releases from waste tanks. When the tank ventilation rate is known, the measured concentrations can be integrated over time to determine a volume of gas released by the tank. This method has a higher degree of confidence on DSTs and positively ventilated single-shell tanks (SSTs) because the ventilation rates are more clearly understood than on passively ventilated SSTs. By careful analysis of the rate of decay of hydrogen concentration following an episodic gas release, an approximate ventilation rate can be derived for any tank.



Composition of Released Gas - Depending upon the specific analysis equipment installed in the SHMS, or by means of off-line analysis of the SHMS samples, quantitative compositional data can be obtained from the sampled atmosphere. The gas compositional data provided by the SHMS can be compared to the known atmospheric composition. Assuming that no other gas sources are present, the ratios of the non-atmospheric components in a tank's atmosphere are equal to the ratios of those components in the gas released directly from the waste.

Frequency of Gas Releases - The data obtained by way of the SHMS provides the information upon which more detailed analysis of a tank's gas release behavior is based. This includes developing a statistical data population from which the frequency and magnitude of a tank's gas releases can be determined. Thus, continuous operation of the installed SHMS permits the frequency of gas releases to be determined. This can be achieved because the significant data population provided by the SHMS is large enough to allow discrimination between component concentration differences between random variation and an actual gas release event.

## 2.2.2 Monitor the Steady State Behavior of Waste Tanks

Continuous monitoring by the SHMS allows time variations in flammable gas concentrations to be determined. Over long time spans these concentrations can be multiplied by the known ventilation flow rates and integrated to determine any variation in the gas release rates and allowing a steady state gas release baseline to be established. This information is used to validate gas generation calculations. Steady state release rates are used to predict the time to flammable concentrations on loss of ventilation.

## 2.3 REGULATORY REQUIREMENTS

Public Law 101-510, Section 3137, SAFETY MEASURES FOR WASTE TANKS AT HANFORD NUCLEAR RESERVATION, known more commonly as the Wyden bill, mandated special procedures to be implemented on Hanford waste tanks deemed at high risk for potential failure mechanisms: "... the Secretary shall determine whether continuous monitoring is being carried out to detect a release or excessive temperature or pressure at each tank so identified. If such monitoring is not being carried out, as soon as practicable the Secretary shall install such monitoring, but only if a type of monitoring that does not itself increase the danger of a release can be installed."

The use of the SHMS has been established as a baseline monitoring device in accordance with the requirements of the Wyden bill. The recognition of this position formed the basis for establishing specific milestones under the Hanford Facility Agreement and Consent Order, also known as the Tri-Party Agreement (TPA). Part of the strategy for dealing with flammable gas generating tanks is elucidated by the TPA milestone M-40-10, "Complete Vapor Space Monitoring for all Flammable Gas Generating Tanks,"

Design, procure, and fabricate standard hydrogen monitoring systems (SHMS) for all unreviewed safety question (USQ) flammable gas generating tanks. Prepare all required safety and environmental documentation for tank intrusive work on a tank by tank or group by group basis. Install the SHMS and obtain vapor space grab samples. Analyze samples using a high sensitivity mass spectrometer to determine the concentration of flammable gases (hydrogen, nitrous oxide, ammonia) for all tanks and the background gas compositions for the double shell tanks that entrap and periodically release gas. The vapor space of each tank will be observed over a sufficient period of time to make decisions regarding resolution of the safety issue. A report, with the analytical data for each tank, will be prepared, cleared for public release, and transmitted to RL for subsequent issuance to the Washington Department of Ecology and Environmental Protection Agency. Monitoring will continue after the initial report.

Gas monitoring is a key to understanding the nature, and thus the risks, associated with flammable gas tanks. The U.S. General Accounting Office (Rezendes 1996) acknowledges flammable gas monitoring as "The primary means of early warning of changes in the flammable gas tanks' status is through continuous temperature and flammable gas sampling (DOE is also installing monitors that detect the presence of flammable gases in tanks)." Johnson (1997) details the major milestones assigned to the Flammable Gas Project by the TPA, as well as by other stakeholder agencies or regulatory agreements. Therefore gas monitoring is integral to achievement of the associated requirement of TPA Milestone M-40-00. While Milestone M-40-10 is considered complete, continued flammable gas monitoring is required to meet the intent of obtaining the best possible information upon which to base decisions regarding the closure of the flammable gas safety issue.

### 3.0 APPROACH TO GAS MONITORING

There are numerous ways to obtain the information identified in Section 2.0. This section discusses the various options including how and where these options apply.

#### 3.1 STANDARD HYDROGEN MONITORING SYSTEM - THE PRIMARY TOOL

The SHMS consists of various analysis instruments and sampling equipment. The basic components include hydrogen specific monitors, a grab sampling apparatus that provides for both automatic and manual operation, and the equipment which support their operation. The SHMS continuously passes air from a tank's atmosphere through a grab sampling apparatus and in-line analysis equipment and returns it to the tank. SHMS are known by a variety of designations based upon the specific configuration of the equipment it contains.

### 3.2 OPTIONS FOR GAS MONITORING

#### 3.2.1 Standard Hydrogen Monitoring System Grab Sampling Equipment

The SHMS are equipped with an electromechanical device that can automatically isolate a volume of the tank's atmosphere in a sample flask upon detection of a hydrogen concentration in excess of the setpoint. The grab sample can be removed from the SHMS and transported to a laboratory for further analysis.

#### 3.2.2 Standard Hydrogen Monitoring System Analysis Equipment

The basic on-line instrument in the SHMS is the Whittaker™ (Trademark of Whittaker Corp.) electrochemical cell. These instruments detect hydrogen concentrations in the sampled atmosphere. The current Whittaker™ cell equipped SHMS contain two cells, with each cell configured to optimally respond in a specific range of hydrogen concentrations. One is identified as low-range, 0 - 1% hydrogen, while the high range instrument measures 0 - 10% hydrogen. A SHMS configured with both the two Whittaker™ cells and the automatic grab sampling capability is known as the SHMS-B. Most of these SHMS transmit the Whittaker™ cell output data continuously to the Tank Monitoring and Control System (TMACS). Other instruments may be added to the base SHMS-B configuration. Most of the installed SHMS in the tank farms are of the SHMS-B configuration. These include tanks 241-A-101, AN-103, AN-105, AN-107, AW-101, AX-101, AX-103, BY-103, S-102, S-107, S-111, S-112, SX-101, SX-102, SX-103, SX-104, SX-105, SX-106, SX-109, T-110, U-102, U-103, U-107, U-108, and U-109.

A SHMS-C adds a dual column gas chromatograph with thermal conductivity detectors (GC-TCD) to the basic SHMS-B configuration. The dual column GC-TCD is configured to analyze hydrogen and has much greater sensitivity than do the Whittaker™ cells. The dual column GC-TCD is used to accurately record baseline hydrogen concentrations typically on the order a few parts per million in the ventilated tanks. SHMS-C are currently installed on tanks 241-AN-104, AY-102, and C-106.

A SHMS-D adds a Bruel and Kjaer photo-acoustic infrared gas analyzer to the basic SHMS-B configuration. The photo-acoustic infrared gas analyzer is used specifically to monitor ammonia concentrations in the atmospheres of the DSTs. SHMS-D are currently installed on the ventilation system exhaust stacks of the AN and AW tank farms.

A SHMS-E+ adds both the dual column GC-TCD and the photo-acoustic infrared gas analyzer to the basic SHMS-B configuration. In addition to hydrogen and ammonia analysis capabilities provided by the Whittaker™ electrochemical cells and the photo-acoustic infrared gas analyzer, the dual column GC-TCD is configured to analyze nitrous oxide, methane, and hydrogen. SHMS-E+ is the latest configuration of the SHMS and is either installed or slated for installation on tanks 241-AN-101, BY-105, S-106, S-109, SX-103,

SY-102, and U-105. A configuration known as the SHMS-E duplicates that of the SHMS-E+ except that the dual column GC-TCD and the photo-acoustic infrared gas analyzer are not installed in the instrument. SHMS-E are either installed or slated for installation on tanks 241-AW-104, AZ-101, AZ-102, S-101, and U-105.

Other specialized gas monitoring equipment configurations exist. A gas characterization system (GCS) contains a Fourier Transform Infrared Spectrometer (FTIR), two dual column GC-TCD's, and a grab sample station. One of the dual column GC-TCD's is configured to analyze hydrogen while the other is configured to analyze nitrous oxide and methane. The FTIR provides analysis of ammonia and can produce infrared spectra of other gaseous components. The grab sample station allows for the remote analysis of tank atmospheric samples. The GCS is a more capable analysis system than the various SHMS configurations. Currently, GCS's are installed on tanks 241-AN-105 and AW-101. Besides various SHMS installations, tank 241-SY-101 is also fitted with a specialized equipment installation known as the Gas Monitoring System (GMS). Wilkins (1997) provides detailed information on the specifics and interpretation of SHMS use.

### 3.2.3 Sample Gas Conditioners

Some SHMS used in high moisture content applications are fitted with Sample Gas Conditioners (SGCs) which prevent the precipitation of water vapor within the SHMS equipment. The SGCs are intended to prevent water condensation from interfering with obtaining a sample or otherwise altering the conditions in which the sample is obtained.

### 3.3 GRAB SAMPLE FREQUENCIES

As part of the monitoring program, grab samples are taken monthly from each DST equipped with a SHMS provided it is not also equipped with a GCS or GMS, and quarterly from each SST with a SHMS. The samples are obtained to check calibration of the SHMS instruments and to track the changes in concentration of nitrous oxide. DSTs are checked more frequently due to the greater risk posed by these tanks for a potential large gas release. Grab samples are not taken from tanks 241-AN-105, AW-101, and SY-101 since these tanks are equipped with on-line instrumentation that provides the same function as the grab sampling.

### 3.4 INTERFACE WITH VAPOR MONITORING PROGRAM

The Hanford Tank Vapor Monitoring Program provides a mechanism by which detailed atmospheric characterization data can be obtained from a tank even though no SHMS is installed on it. The portable vapor sampling equipment is used to obtain grab samples of a tank's atmosphere. These samples can then be transported to a laboratory for analysis. The sample containers used are SUMMA™ (Trademark of Moleetrics, Inc.) trap vacuum canisters and sorbent tube

columns. The design of the equipment and the sampling techniques employed have been refined over years of operational experience at the Hanford site to maximize assurance that a representative atmospheric sample is captured by the grab sampling containers.

These sampling and analysis techniques offer increased speciation and resolution of gaseous components present in an atmospheric sample. The information obtained via these methods is utilized by the Flammable Gas Safety Program, which makes appropriate responses to the reported data. If the Vapor Monitoring Program reports a significant fuel concentration, a dedicated SHMS may be installed on the subject tank for follow-up monitoring.

### 3.5 RELATIONSHIP TO RETAINED GAS SAMPLER/DRILL-STRING GASES

The retained gas sampler (RGS) obtains a sample of waste tank contents including retained gases in-situ. A sample obtained by this method represents the gas composition that is generated and trapped in the tank wastes. When not diluted by the nitrogen purge, the same relationship applies for drill string gases obtained during waste tank core sampling. Data from the RGS or drill string gas samples can be used to further establish the concentration ratios of the gases produced by the tank wastes.

### 4.0 DETERMINATION OF THE LOWER FLAMMABILITY LIMIT

In this section we discuss the gases of concern, the associated Lower Flammability Limit (LFL) of the individual gases in air, the LFL of mixtures and effects of nitrous oxide on the LFL in the presence of other oxidizers. The actual compositions of waste gases are presented and a recommendation for the setpoint for alarms on the SHMS is established.

#### 4.1 LOWER FLAMMABILITY LIMITS FOR INDIVIDUAL GASES OF CONCERN

The LFLs of individual flammable gases depend upon the direction of the advancing flame front. When these speeds are low, as they are during combustion at lean flammability limits, convection currents generated in the combusting gas mixture can have a greater velocity than the flame front. The energy released during combustion heats the surrounding gas and lowers its density. Because of the decreased density, the heated air experiences free convection upwards due to the buoyancy forces acting on the heated gas volume. In order for combustion to continue at a specific location, the burning velocity must equal or exceed the velocity at which the gases are convecting upwards. Thus the mixture can be flammable if the flame front advances upward while simultaneously being non-flammable if the flame front must advance in the downward direction.

Accordingly, a flame front can propagate upwards at a lower fuel concentration than it can downwards due to the upward convection caused by the warmer gases

resulting from the reaction. To be flammable in the downward direction, the flame speed must exceed the velocity at which the local gases are convecting upwards. This equates to a flame speed that must be  $\geq 4$  cm/sec. In addition, turbulent mixtures exhibit lower LFLs than do quiescent mixtures. Recent studies indicate that the flame speed upper bound in any well-mixed Hanford tank headspace will be no more than 5m/sec (Zerkle 1997).

Hydrogen is the predominant fuel gas produced by the Hanford waste tanks. For quiescent hydrogen-air mixtures, the upward propagating limit (UPL) LFL is about 5% hydrogen and the downward propagating limit (DPL) LFL is 8% hydrogen. For turbulent mixtures, the UPL LFL is about 4% hydrogen and the DPL LFL is 6% hydrogen (Cashdollar 1992).

Ammonia is the other fuel constituent which, under certain conditions, can account for a sizable fraction of the released gas composition. Ammonia is attributed with a UPL LFL of 15%, which is not qualified as to the presence of a turbulent mixture (Pfahl and Shepherd 1997). Methane possesses a UPL LFL of 5% (Pfahl and Shepherd 1997). Total non-methane hydrocarbons (TNMHC) are attributed with a UPL LFL of approximately 2.2% for alkanes and 2.5% for alkenes assuming a mean molecular weight of 42 (Zabetakis 1965). While carbon monoxide has been detected as very low concentrations in a few tanks, it is believed to originate from vehicle exhaust entering the tank. No mechanisms have been identified which would produce carbon monoxide in the waste. Carbon monoxide will not be considered further as a waste generated flammable gas.

The LFL is taken to be the lowest fuel concentration in any combination of these conditions which is flammable. Therefore, the LFL is considered the flammable limit at the upward propagating, turbulent condition. The temperature effect on the required concentration of flammable species in turbulent mixtures at the LFL is shown in Table 1. For all the fuel species of interest in the temperature ranges of interest, the relationships are linear. At a certain limiting temperature, the required fuel concentration in the mixture reaches zero at the LFL. For example, the concentration of paraffin fuels at the LFL of an air-paraffin mixture is zero for any temperature above about 2,400°F. In essence, at the limiting temperatures the fuels are unstable and spontaneously combust to their normal reaction products at any concentration so long as an oxidizer is present. It can also be observed from Table 1 that any variation of the fuel concentrations at LFL with temperature will be negligible over the temperature ranges of the Hanford waste tanks.

Table 1: Flammability Limits of Pure Component - Air Mixtures

Fuel	UPL(%)	DPL(%)	LFL-Temperature Relationship
H <sub>2</sub>	4	8	$LFL @ T_2 = 4 * [1.00 - 1.15 * 10^{-3} * (T_2 - 77^\circ F)]^2$
NH <sub>3</sub>	15	16	$LFL @ T_2 = 15 * [1.00 - 3.33 * 10^{-4} * (T_2 - 77^\circ F)]^2$
CH <sub>4</sub>	5	6	$LFL @ T_2 = 5 * [1.00 - 4.40 * 10^{-4} * (T_2 - 77^\circ F)]^3$
TNMHC <sup>1</sup>	2.5	?	$LFL @ T_2 = 2.5 * [1.00 - 4.33 * 10^{-4} * (T_2 - 77^\circ F)]^3$

<sup>1</sup> TNMHC is attributed with a UPL LFL of 42 grams/m<sup>3</sup>. The 2.5% value assumes that the mean molecular weight of TNMHC is 42 (e.g., C<sub>3</sub>H<sub>6</sub>)

<sup>2</sup> derived from Coward and Jones, 1952

<sup>3</sup> Zabetakis, 1965

#### 4.2 LOWER FLAMMABILITY LIMITS OF GAS MIXTURES

The body of current work on gas flammability issues in the tank farm waste tanks suggests that of the gas components (nitrogen, nitrous oxide, hydrogen, ammonia, methane, and TNMHC) only hydrogen and ammonia are significant in determining the lean flammability limits and are therefore the main concerns. Hydrogen is the dominant contributor to the fuel content of the released gases. Ammonia also contributes noticeably to the fuel content to the gas mixture, but due to the known complexity of reactions involving ammonia, it is difficult to determine the change in propagation reaction speeds when ammonia combustion is involved. In these fuel mixtures, 1% ammonia represents a fuel content equivalent to about 0.3% hydrogen. Although methane is often detected in the gases produced by the Hanford waste tanks, it rarely exceeds a few percent of the total quantity produced. At these low concentrations, despite the fact that methane is an energetic fuel, methane has an insignificant effect on the resulting flammable level of the gas mixture. The only other reactive fuel constituent found in the gases is TNMHC. All the carbon-containing fuels are less prevalent than hydrogen (i.e., ≤ 5% of the total composition of the released gas). In all SSTs measured to date, the methane concentration has not exceeded 150 ppmv (Barker et. al., 1998). TNMHC shows still smaller concentrations. The sum of the hydrocarbon fuel gases is present in such small amounts that their effect on flammability levels is negligible.

Nitrous oxide and nitrogen are present in significant quantities in waste tank gases. The nitrogen is unreactive and serves to dilute the fuel concentration of the released gas. If present in sufficient concentrations, nitrogen may lower the fuel-oxidizer concentration sufficiently that the otherwise flammable mixture becomes inerted. Depending on the fuel species in the mixture, this occurs at about 60% to 80% nitrogen (Pfahl & Shepherd, 1997). When high concentrations of nitrous oxide are present in fuel mixtures

(approximately 1:1:1 ratio of hydrogen, nitrous oxide, and air), and certain restrictive conditions on temperature and ignition energy are met, it is capable of dissociation or spontaneous decomposition (Cashdollar, et. al. 1992). When nitrous oxide is present in combustng mixtures containing ammonia or methane based fuels, most of the nitrous oxide present will energetically dissociate during the combustion reaction. In the presence of a purely hydrogen based fuel mixture undergoing combustion, nitrous oxide is essentially unreactive, particularly in leaner mixtures. Because the concentrations of ammonia and methane in waste gases are so much lower than the hydrogen concentrations, nitrous oxide has consistently been found to have little or no effect on altering the LFL of these fuel mixtures. Additionally, both humidity and temperature have been found to have no significant effect on lean flammability limits of hydrogen-ammonia-nitrous oxide mixtures (Akbar et. al. 1997; Breshears et. al. 1997; Pfahl and Shepherd 1997).

These studies have consistently shown that nitrous oxide serves only to dilute the flammable concentration that the hydrogen would otherwise create in a tank headspace. The studies all point to the difficulty in understanding the affect of multiple oxidizers, in particular nitrous oxide, on flammability limits. It is generally noted that nitrous oxide can play a more significant role in determining flammability limits in mixtures based on a fuel of ammonia or methane, but it contributes essentially nothing to flammable mixtures with hydrogen as the fuel. Because of the predominance of hydrogen as the fuel in waste tank atmospheres, the conclusion of the inerting effect of nitrous oxide naturally follows.

An additional point regarding the presence of nitrous oxide in hydrogen and ammonia fuel mixtures is that the nitrous oxide lowers the flame speeds in such combustng mixtures (Breshears et. al. 1997). The reduction in flame speed serves to both reduce the hazard of combustion while tending to increase the flammable limits of such mixtures. Because hydrogen is the dominant fuel in the Hanford waste tank gases, the presence of nitrous oxide contributes insignificantly to the flammable hazard, and therefore the flammable level, of the gases (Breshears, et. al., 1997). Additionally, concentrations of nitrous oxide conducive to its dissociation are unlikely to occur in the Hanford waste tanks except perhaps in the most limiting and severe episodic release scenarios.

To summarize the effect of nitrous oxide and nitrogen, the presence of these components in released gas serves to dilute any resulting fuel concentration in a tank's headspace. In the vast majority of cases, including all situations ever measured directly at Hanford, nitrous oxide and nitrogen act as diluents when the associated fuel gas mixture is near the LFL (Barker et. al., 1998).

The exact composition of gas released from any one tank will vary from that of another tank, but generalized gas compositions can be stated which will encompass the vast majority of any released gases. Episodic release mechanisms, which predominate in DSTs, tend to produce higher ammonia compositions than steady state releases, which predominate in SSTs. This



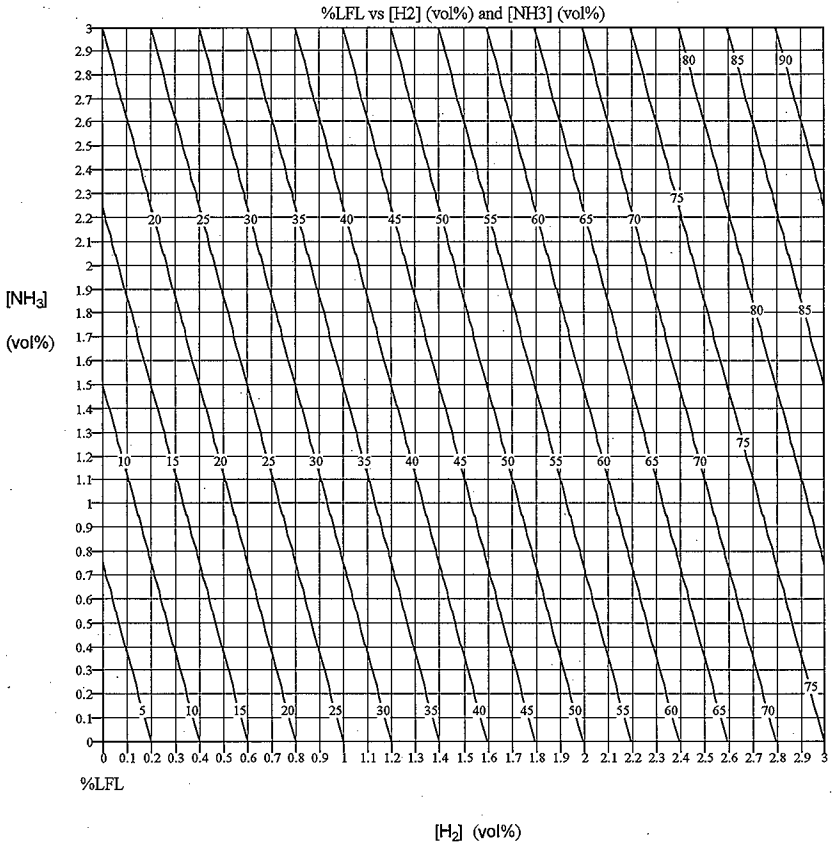
results because the convective action of episodic releases force waste from deep in the tank to the surface, creating a larger concentration gradient for the mass transfer of ammonia across the waste-air interface. In SSTs, the ammonia concentration at the waste surface is depleted compared to a DST that has recently experienced a buoyant displacement gas release event. (Barker et. al., 1998).

The chemical equilibrium of ammonia in aqueous solutions favors the release of gaseous ammonia at higher temperatures and higher pH values (i.e., higher hydroxide concentrations) (Akbar et. al., 1997). Although the combustion reactions involving hydrogen and ammonia along with the disassociation of nitrous oxide are exothermic, the reaction rates and associated flame speeds are not necessarily fast enough to present a deflagration hazard. If the released gas were pure hydrogen, at fuel concentrations of  $\leq 7\%$ , the gas mixture will either be nonflammable, or possess a minuscule flame speed which would not present an explosion hazard (Breshears, et. al., 1997). The required fuel concentrations at the LFL of hydrogen-ammonia-nitrous oxide mixtures are reduced with increased physical agitation of the gas mixtures and increased ignition energies (Pfahl & Shepherd, 1997; Cashdollar et. al., 1992).

In summary, hydrogen and ammonia are the key components in determining the flammable limits of the waste tank fuel gases in air, when the fuel gases originate from the Hanford waste tanks. The relationship of hydrogen and ammonia to flammable levels in air are linear at the lower concentrations and the UPL-LFL of mixtures can be expressed as a linear combination of each of the component relationships. The fuel/air mixture - LFL relationships are illustrated in Figure 1 for hydrogen and ammonia concentrations from 0.0 to 3.0 volume percent. This plot is a graphical representation of Le Chateliers' Linear Mixing Law assuming that hydrogen and ammonia are the only fuel sources present:

$$\%LFL = 100 * [(vol\% \text{ hydrogen} \div 4.0 \text{ vol}\%) + (vol\% \text{ ammonia} \div 15.0 \text{ vol}\%)]$$

Figure 1: Atmospheric Fuel Content vs. H<sub>2</sub> and NH<sub>3</sub> Concentrations



#### 4.3 LOWER FLAMMABILITY LIMITS USING RETAINED GAS SAMPLER DATA

The Retained Gas Sampler (RGS) has been employed on a number of tanks at the Hanford site, including several DSTs. The compositions of gas generated by the waste usually possess sufficiently high concentration of fuel (hydrogen and ammonia) and oxidizer (nitrous oxide) that the gas is itself flammable. If this gas is released in a rapid fashion from one particular location in the waste, a plume of undiluted waste gas could form for short periods of time within the tank headspace. If a rapid release of gas were large enough, as might result from a significant buoyancy induced waste displacement event, there may temporarily be an insufficient volume of air in the tank headspace to inert the resulting gas mixture. Additionally, the plume burn scenario involves the concept of direct combustion of the undiluted released gases, or released gases not yet diluted to inertness. The undiluted waste gas compositions have been measured in some SSTs and DSTs by the Retained Gas Sampler (RGS), a technique for obtaining an in-situ gas sample from the waste.

Measured gas compositions are listed in Table 2. Table 2 values, except those for 241-SY-101, represent the composition of the waste gases as they are contained in the waste. They also represent the limiting plume concentration. In contrast, the values for tank 241-SY-101 represent the best estimated gas composition resulting from a large episodic release of gas due to a density instability within the tank's waste. The significant agitation associated with such an event brings waste with higher dissolved ammonia concentrations to the regions closer to the surface. During steady conditions, the ammonia concentrations in the waste near the surface are depleted relative to the bulk waste ammonia concentrations by means of diffusion to the tank atmosphere. Therefore, in a density instability gas release event, large amounts of ammonia rich waste are immediately placed at or adjacent to the waste surface. The highest ammonia concentrations detected in a tank atmosphere have been about 15,000 ppmv (1.5%) in tank SY-101 (Barker et. al., 1998). This corresponds to about 500 ft<sup>3</sup> released over a short period of time. Assuming the maximum episodic gas release from tank SY-101 of 12,000 ft<sup>3</sup> (Biehl et. al. 1994), this shows that about 4% of the total released gas volume was ammonia. Table 3 indicates the resulting hydrogen and ammonia concentrations at the LFL assuming that these components are present at the ratios given, which is equivalent to the fuel gas ratios indicated in Table 2.

Table 2: In-Situ Waste Tank Gas Compositions Component Percentage

Tank	H <sub>2</sub>	N <sub>2</sub> O	N <sub>2</sub>	NH <sub>3</sub>	CH <sub>4</sub> +TNMHC
241-A-101 <sup>1,R</sup>	75	5.6	16	2.4	2.5
241-AN-103 <sup>1,R</sup>	62	3.8	33	0.06	0.9
241-AN-104 <sup>1,P</sup>	47	20	31	0.02	1.3
241-AN-105 <sup>1,R</sup>	62	12	25	0.02	0.9
241-AW-101 <sup>1,R</sup>	31	7.1	58	0.02	3.3
241-BY-109 <sup>2,P</sup>	50	18	29	0.06	3.1
241-S-106 <sup>2,P</sup>	63	11	24	0.41	0.73
241-SY-101 <sup>3,F</sup>	29	24	33	0.14	1.0
241-U-103 <sup>2,F</sup>	22	40	35	11.0	1.0
$\mu^4$ :	49	16	32	1.7	1.6
$\pm\sigma^5$ :	$\pm 17$	$\pm 11$	$\pm 11$	$\pm 3.4$	$\pm 1.0$

<sup>1</sup> (Shekarriz, et. al. 1997) derived from RGS results

<sup>2</sup> (Mahoney 1997) derived from RGS results

<sup>3</sup> (Biehl, et. al. 1994) best estimate of episodic release gas composition average

<sup>5</sup> standard deviation of listed  $\mu$  values (does not include  $\sigma$  reported for individual  $\mu$  values in the References).

<sup>R,P,F</sup> (Pfahl and Shepherd 1997) present flammability findings from various researchers for hydrogen-nitrogen-nitrous oxide-air mixtures which can be compared to the listed compositions. These tabulated compositions can be specified as: (R) fuel rich and thus not flammable; (P) potentially flammable with an ignition source of sufficiently high energy (> 20 joules); or (F) flammable.

#### 4.4 LOWER FLAMMABILITY LIMIT ALARM SETPOINTS

The SHMS have alarms with interlocked automatic grab sampling capabilities. In order for these features to operate a setpoint for the alarm must be specified. The original issue of this document established a setpoint based on an assumed worst case flammable gas mixture containing approximately 2% ammonia and 2.5% hydrogen. In addition, the values for the LFL of the mixture were based on the lowest values reported in the literature rather than standard values commonly accepted. This approach establishes a conservative alarm setpoint with respect to 25% of the LFL. The hydrogen from this mixture was multiplied by 25% as suggested by the National Fire Protection Association and converted to parts per million by volume (ppmv) resulting in a setpoint of 6250 ppmv hydrogen.

Table 3: Calculated Flammable Levels for Measured Headspace Concentrations<sup>a</sup>

Tank	[H <sub>2</sub> ] ppmv	[NH <sub>3</sub> ] ppmv	Associated %LFL
A-101	1,040	753.8	3.1
AN-103	3,000	200 <sup>b</sup>	7.6
AN-104	6,109	200 <sup>b</sup>	15
AN-105	17,000	610	43
AW-101	8,800	19	22
BY-109	650	40	1.7
S-106	20	36.5	0.074
SY-101	53,000	13,000	140
U-103	1,230	730.2	3.6

<sup>a</sup> LFL values derived from Le Chateliers' Linear Mixing Law assuming that H<sub>2</sub> and NH<sub>3</sub> are the only flammable species present in a tank headspace, with the ratio of concentrations of H<sub>2</sub> and NH<sub>3</sub> at the LFL given by Table 2.

<sup>b</sup> ammonia values based upon concentration in RGS

Experience to date with this setpoint is that it does not result in nuisance alarms by being too low and if anything results in too few automatic grab samples being trapped. All SHMS are currently set to this value and a change from it would result in unwarranted costs. Therefore, it is recommended that the setpoint remain unchanged at 6250 ppmv. Because 25% of the LFL based on hydrogen is 10000 ppmv, and because the highest ammonia to hydrogen ratio measured in any tank headspace is no more than about 0.3, it is highly unlikely that a 25% LFL condition could exist without the 6250 ppmv setpoint being achieved. This value should be viewed only as an alarm setpoint and not related to 25% of the LFL. In the event of an alarm, the actual percent of LFL can be calculated based on measured flammable gas concentrations rather than assumed gas ratios.

## 5.0 RESPONSE ACTIONS

The TWRS operational actions in response to the presence of flammable gas in the tank dome space are specified by the TWRS Basis for Interim Operations (BIO) (HNF-SD-WM-BIO-001, Appendix B of Appendix E, FLAMMABLE GAS JCO CONTROLS) and the associated Technical Safety Requirements (TSR's) (HNF-SD-WM-TSR-006, section 3.2 - FLAMMABLE GAS). These requirements specify actions for DST and Aging Waste Facility Tank Ventilation Systems, SST Ventilation Systems, both active and passive, DCRT Ventilation Systems, and the 244-AR TK-002 Ventilation System. For the details of the operational responses the reader is referred to these documents.

In addition to the operational responses in the field, the detection of elevated levels of flammable gas in the tank dome space require investigation to understand if tank conditions have fundamentally changed or if any long term changes need to be made to the tank operating conditions. These investigations are triggered by detection of flammable gas concentrations in the tank dome space which are greater than 25%, and again if greater than 100%, of the UPL LFL for the gas mixture found in the tank.

## 5.1 RESPONSE TO FLAMMABLE GAS CONCENTRATIONS GREATER THAN 25% OF THE LOWER FLAMMABILITY LIMIT

Upon detection of a condition where a tank dome space is shown to be above 25% of the UPL LFL an investigation of the tank conditions shall be initiated. This investigation will focus on understanding why the tank produced the condition, understanding the maximum flammable gas release likely in the tank and an evaluation of potential mitigative actions to assure the condition does not worsen.

At the writing of this document, only three tanks, 241-SY-101, AW-101, and AN-105, have shown conditions above 25% of the UPL LFL. This condition has been associated with a gas release event and has persisted for fairly short periods of time. The necessary investigations have been completed and mitigative actions are in place. For any other tank that may exceed 25% of

the UPL LFL in the future, consideration shall be given to better characterize the tank flammable gas retention by:

- Adding a GCS to the SHMS to provide more complete understanding of gas composition.
- Deployment of the Void Fraction Instrument, the ball rheometer, and/or the retained gas sampler to obtain data on flammable gas volume, composition, and location.
- Visual investigation of the tank surface through either photographic or video techniques. This observation may reveal clues to the nature of the release such as whether the phenomena were localized in a plume release.

The evaluation of mitigation of the flammable gas hazards should, as a minimum, address reducing the inventory of flammable gas available, change conditions to make release events smaller, and reducing the time at risk in the tank dome space. Any recommended mitigative actions should be based on cost/benefit considerations and criteria developed as part of the study.

## **5.2 RESPONSE TO FLAMMABLE GAS CONCENTRATIONS GREATER THAN 100% OF THE LOWER FLAMMABILITY LIMIT**

Only one tank, 241-SY-101, has shown this condition. Upon detection of a flammable gas concentration in a tank dome space above 100% of the UPL LFL (not including small localized plumes), tank specific mitigative measures to assure the condition does not re-occur should be implemented in addition to the actions specified previously in section 5.1.

## **6.0 DURATION OF MONITORING AND BASIS FOR REMOVAL OF GAS MONITORING EQUIPMENT**

The operation of SHMS and other gas monitoring equipment incurs a significant cost to the plant. In order to minimize this cost, a basis for when to discontinue gas monitoring is needed. In this section we will discuss the length of time gas monitoring must continue on a tank, the requirements that drive gas monitoring and the basis for removal of the monitoring system.

It should be noted that these are minimum requirements associated with long term tank atmospheric monitoring for flammable gas.

## 6.1 MINIMUM MONITORING DURATION

Before a permanent SHMS installation can be removed from a tank, all of the following conditions must be met:

- Flammable Gas Watch List Requirement: The tank must not be on the flammable gas watch list.
- Monitoring Time Requirement: At least 36 months of data must be collected.
- Gas Release Event Requirement: If the data show significant gas release events occurring in the tank, further requirements must be met. A significant gas release event is defined as a characteristic increase in tank hydrogen concentration of at least 500 ppmv followed by exponential decay in the concentration. This should not be confused with seasonal increases and decreases in concentration or with drift in the instrument baseline. If one or more significant gas release events have been detected, at least 24 consecutive months of data since the last event must be collected within the total 36-month monitoring period. During the subsequent 24-month period, significant gas release events must not occur in the tank.

If the above conditions are not met, monitoring will continue on a tank until these conditions are met.

The watch list requirement is driven by the interpretation of the Wyden Bill requirements for monitoring the tanks. The monitoring time requirement is to provide sufficient monitoring information to establish a basis that the tank does not pose a significant hazard due to release of flammable gas. The gas release event requirement is provided to establish statistically significant frequency distributions for tanks which exhibit episodic gas release behavior. The latter requirement includes phased criteria to provide a means to remove SHMS from a tank which was once known to possess, but no longer exhibits, periodic gas release behavior.

In addition to the above requirements, a permanently installed SHMS should not be removed if significant operational activities are planned in the tank. Examples of significant operational activities are: salt well pumping, core sampling, major transfers, etc..

## 6.2 PORTABLE STANDARD HYDROGEN MONITORING SYSTEMS

Trailer mounted SHMS are available in the tank farm for temporary monitoring of the flammable gas conditions of a tank. They should generally be used whenever a globally waste disturbing activity is planned. As a general rule, once a temporary SHMS has been connected to a tank it should remain there until the condition it was installed to monitor is no longer a concern and the tank has established a baseline steady state flammable gas concentration.



Each such installation should separately document the criteria for monitoring and removal of monitoring associated with the installation.

## 7.0 CONCLUSIONS

This revision briefly surveyed much of the results on the contemporary gas generation/release behavior studies that add confidence in the use of 6,250 ppmv hydrogen as the definition of the 25% LFL alarm setpoint. Experience and analysis both illustrate that this value is conservative, provides the necessary control, and should continue to be used as the SHMS alarm and programmatic decision setpoint. Evolving concerns and response requirements have created changes in the way waste tank gas concentrations must be monitored at the Hanford site. It is now a requirement for SHMS monitoring on all Flammable Gas Watch List tanks as well as all tanks involved in waste transfer planning and activities. Continued study of the waste tank gas generation phenomena has refined estimates of the types and concentrations of gases being released by the tanks, as well as properties of these gas mixtures. Operations and programmatic actions upon detection of a 25% LFL condition are summarized.

Finally, the criteria for termination of SHMS monitoring on a tank was stated:

- The tank must not be on the flammable gas watch list.
- At least 36 months of data must be collected.
- No periodic gas release events have occurred over the last 24 months.

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