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Volatilization and Flammability Characteristics of Elemental and Organic Mercury

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1 Summary of Revisions

5/12/2015 Revision 0: Initial Issue
5/19/2015 Revision 1: Revised discussion for clarification with no impact to conclusions of the evaluation.
6/8/2015 Revision 2: Revised wording and added Executive Summary for clarification with no impact to conclusions of the evaluation.

2 Purpose

This evaluation investigates and discusses the chemical characteristics with respect to volatility and flammability of potential organomercury compounds.

3 Introduction

Mercury is one of the most toxic elements to human health. All mercury species are toxic. Mercury is insoluble in water and soluble in nitric acid and easily alloys with many other metals producing amalgams. Mercury can exist naturally as elemental, oxidized inorganic (mercuric or mercurous) mercury, or oxidized organic (methyl/ethyl mercury) forms. Mercury evaporation rate, governed by the vapor pressure, depends on the volatility of the compound and the associated temperature. Mercury compounds can vary significantly in their vapor pressure and volatility such that physicochemical changes affect the phase concentration [Ref. 8.18].

Current accident scenarios related to the Saltstone facility assume that methyl mercury (II) compounds possess the same chemical properties as dimethyl mercury. Thus, it has been categorized as having the same volatility. This is an overestimation of the impacts of this mercury complex. In fact, methyl mercury (II) compounds will not volatilize, nor are they flammable. With the inability to volatilize, methyl mercury compounds will also not impact vapor space flammability. This evaluation will address potential methyl mercury compounds in SRS waste and identify the known mercury species that do pose a flammability concern.

4 Executive Summary

- The dominant organomercury compound found in the Tank Farm is the methyl mercury (II) cation as a hydroxide or nitrate salt. These compounds are not volatile and do not contribute to flammability.
- Dimethyl mercury has been detected in Tank 50 sample results (See Section 6.3) but at significantly lower concentrations than the methyl mercury (II) cation. Dimethyl mercury is a volatile species and is the only identified mercury compound of flammability concern.
- The Lower Flammability Limit (LFL) for dimethyl mercury was conservatively calculated as 2.5% (See Section 6.2.2).

5 Assumptions

5.1 Mercury compounds are categorized by phase according to the applicable melting and boiling points. **Justification:** It is recognized that Reference 8.33 determines the state of each chemical in a boiling liquid waste tank (i.e., ~100°C), for the Saltstone safety basis. To provide a practical method for developing a reasonably conservative source term for the various chemical species the criteria is summarized as follows:

- The chemical is "solid" if its melting point is > 100°C
- The chemical is "liquid" if its melting point is <100°C but its boiling point is >100°C
- The chemical is "volatile" if both its melting point and boiling point are <100°C.

In general, these definitions are used to specify which compounds are considered solid, liquid, or volatile species for chemical consequence analysis, in order to predict the contribution of each species in the vapor space. This does not exclude compounds that are primarily solid or liquid but have a relatively high vapor pressure (i.e., elemental mercury).

5.2 Organomercury vapor concentrations are calculated using the maximum evaporator operating temperatures. **Justification:** The vapor pressure of a compound increases with temperature, thereby increasing the concentration in the vapor space. The evaporators operate at temperatures up to 186°C, thus it is conservative to utilize this operating temperature to bound waste tank and operating temperatures at Saltstone, 115°C and 95°C, respectively [Ref. 8.37, 8.39, & 8.40].

5.3 The bounding LFL of dimethyl mercury was calculated to be 2.5 volume %. **Justification:** Limited experimental data is available for dimethyl mercury due to its toxicity. Consequently, the LFL was calculated. Four separate calculations (Case 1-4) utilizing various chemical correlations and methodologies were performed to determine the most bounding LFL concentration.

5.4 The dimethyl mercury contribution to the LFL bounds all other dialkyl species. **Justification:** Dimethyl mercury is the most abundant dialkyl (R_2Hg) species, where R is an organic radical (i.e., methyl, ethyl, propyl, butyl). The abundance of carbon-containing functional (hydrocarbon) groups is inversely related to their stability. The more stable a functional group is, the less it would dissociate. Stability of straight chained alkyl groups increases in the order methyl < ethyl < propyl < butyl[1] [Ref. 8.31]. Thus, the abundance of the straight chained alkyl groups in waste would be reverse, methyl > ethyl > propyl > butyl. This is applicable to all functional group prefixes (i.e., mono-, di-, tri-, etc.). The methyl radical is the most reactive and least stable, therefore the most likely for alkylation of mercury; consequently, it has the largest or most bounding alkyl and dialkyl concentration. Diethyl mercury has not been measured, but sample analysis has shown that monomethyl mercury (II) cation concentrations are greater than monoethyl mercury concentrations in SRS waste [8.22]; this demonstrates the higher abundance of methyl groups compared to other alkyl groups.

[1] The order specified is derived from the organic radical stability principles of alkanes, where stability increases in the order of methyl < primary < secondary < tertiary [Ref. 8.31].

5.5 The unidentified mercury species in the Eurofins sample(s) will be bound by the impacts of dimethyl mercury on the flammability. **Justification:** Sample analysis measured low (0.0235 mg/L) concentrations of dimethyl mercury [8.19]. According to Assumption 5.4, dimethyl mercury is the most abundant dialkyl species based on stability. Thus, the dimethyl concentration is the most bounding flammable concentration. Section 6.2.2 conservatively calculates the impact of dimethyl mercury on the LFL (i.e., 2.5 volume %). Since all dialkyl species are bound by the dimethyl mercury concentration, their overall contributions on the LFL will be bound by the analysis performed on dimethyl mercury, (Appendix 9.4 calculates the LFL for additional dialkyl species).

5.6 Methyl mercuric nitrate is categorized as a solid. **Justification:** Although a study has shown methyl mercuric nitrate to have a melting point of 100°C, extensive literature research was performed and minimal chemical characteristic information was found. As stated in Assumption 5.1, 100°C falls on the line between a solid and a liquid. As stated in Section 6.2, the organic mercury compound properties will depend upon the nature of the inorganic radical or anion attached. Because the anion is nitrate, the substance is an ionic salt-like compound. Thus, for the purposes of Reference 8.33, this species would fall into the solid category, which is consistent with the other species identified in Table 6-1.

6 Discussion

6.1 Mercury Compounds

Mercury can exist in several methylated forms because it readily forms covalent bonds with organic and inorganic functional groups (see Table 6-1 for the potential forms found in SRS waste streams). The specific state and form of mercury present is dependent upon a number of factors, including redox potential, pH of the media, and temperature. The most reduced form of mercury is elemental mercury, which is a liquid at ambient temperatures, readily volatilizes, and has a high vapor pressure (See Figure 6-1, Table 6-2). Mercury is also easily alkylated by a wide variety of alkyl donors. Due to the availability of methyl donors and the strength of the $Hg\text{-}CH_3$ bond, methylated mercury is the most common mercury form [Ref. 8.4]. In general, alkaline waste solutions can rapidly methylate Hg(II) present in the solution to methyl mercury cation (CH_3Hg^+). Then, more slowly over time, a second methyl group could be added to form dimethyl mercury ($Hg(CH_3)_2$) but at much lower concentrations [Ref. 8.5].

Based on the anticipated chemicals in the liquid waste supernate controlled by the Tank Farm Waste Acceptance Criteria (WAC) [Ref. 8.7], the mercury complexes anticipated to form under normal operations in the waste tanks are identified in Table 6-1. Since these complexes are anticipated, they are discussed in this document. Although not anticipated in the liquid waste system, additional mercury complexes are discussed in Appendix 9.1. The mercury forms in Table 6-1 provide a reasonable assessment against the anticipated impacts on flammability under normal caustic operating conditions.

Table 6-1: Potential Mercury Species found in SRS Liquid Waste Stream [Ref. 8.1, 8.3, 8.4, 8.8 & 8.15].

	Mercury Species					
Parameter	Mercuric Chloride	Methyl Mercuric Chloride	Methyl Mercuric Hydroxide	Methyl Mercuric Nitrate	Dimethyl Mercury	Elemental Mercury
Formula	$HgCl_2$	CH_3HgCl	CH_3HgOH	CH_3HgNO_3	$(CH_3)_2Hg$	Hg^0
CAS #	7487-94-7	115-09-3	1184-57-2	2374-27-8	593-74-8	7439-97-6
Molecular Weight (g/mol)	271.49	251.08	232.63	277.62	230.66	200.59
Specific Gravity (g/mL)	5.44	4.06	α	α	2.96	13.54
M.P. (°C)	277	170	137	100	-43	-38.9
B.P. (°C)	302	sublimates	α	α	93-94	356.6
K_H (unitless) Air/water distribution constant	5.0E-8	5.0E-5	5.48E-09	β	0.3	0.3
Vapor Pressure (at 25°C)	*2.89E-4 mmHg	0.0085 mmHg	0.21 mmHg	β	*62.37 mmHg	*0.0018 mmHg
Reference 8.33 Criteria Specification	Solid	Solid	Solid	Solid γ	Volatile	Liquid
Other	Volatilizes unchanged at 300°C. Highly toxic.	Stable but incompatible with strong oxidizing acids.	Water Solubility = fully miscible (>100 g/L at 25°C) Solid at 25°C and 1 atm.	Water soluble	Stable but flammable and incompatible with strong oxidizing acids.	Water Solubility = 0.00006 g/L (at 25°C)

*Calculated vapor pressure using Reference 8.15.
α No reliable data has been established for this compound, however, this data is not vital for the volatility or flammability determination in this evaluation.
β Extensive literature research was performed and the information identified was not reliable/consistent. However, Section 6.2.1 addresses compound characteristics qualitatively.
γ See Assumption 5.6.
**The species listed above are the most probable species in SRS waste, see Appendix 6.1 to see additional mercury speciation information.

6.2 Volatility

A compound that is volatile readily evaporates under standard temperatures and pressures. The more volatile a compound is, the larger the concentration would be in the vapor space. However, not all volatilized vapors are flammable.

Organomercury compounds can be conveniently classified into two types, RHgX and R_2Hg, where R is an organic radical (e.g., an alkyl group) and X an inorganic anion. RHgX compounds in general are crystalline solids whose properties depend upon the nature of X. When X is chlorine, bromine,

iodine, cyanide, thiocyanide, or hydroxyl, the compound is a covalent substance more soluble in organic liquids than in water. When X is a sulfate, nitrate, phosphate, or perchlorate radical, the substance is an ionic salt-like compound. R_2Hg compounds are non-polar, volatile, toxic liquids or low-melting solids. Dialkyl mercury compounds are thermally unstable and light-sensitive [Ref. 8.30].

The mercury compounds in Table 6-1 are not all volatile or reactive species. Figure 6-1 and Table 6-2 outline a functional list of mercury compounds.

Figure 6-1: Classification of Mercury Compounds [Ref. 8.1]

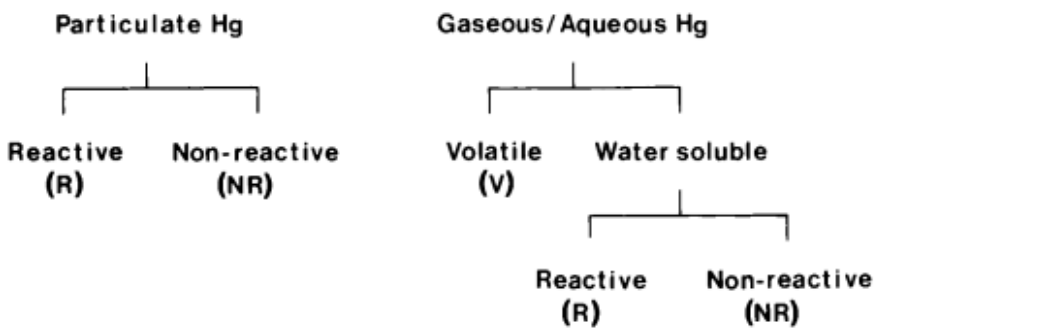

Fig. 1. Classification of mercury compounds according to appearance in nature, but also with respect to possible separation with available sampling and analytical methods.

Table 6-2: Classification of Possible Mercury found in Waste in Figure 6-1 [Ref. 8.1]

Volatile (V)	Reactive (R)	Non-Reactive (NR)
• Hg^0 • $(CH_3)_2Hg$ Relatively high Henry's Law constant	• Hg^{2+} (can complex with organic acids) • HgO (On aerosol particles) • HgX_2 • HgX_3^- • HgX_4^{2-} X = OH^-, Cl^-, and Br^-	• $(CH_3)Hg^+$ • Organomercuric compounds (RHgX) R= CH_3 X = OH^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}, CN^-, ClO_4^-, PO_4^{3-}, I^-, and SCN^-

Figure 6-1 and Table 6-2 represent the classification of mercury compounds based on volatility and reactivity. As shown, elemental (Hg^0) and dimethyl mercury ($(CH_3)_2Hg$) are volatile (V) compounds and can be found as gaseous/aqueous Hg. In contrast, the methyl mercury cation ($(CH_3)Hg^+$) is a non-reactive (NR) compound and can be found as particulate Hg or water soluble gaseous/aqueous Hg.

The likely monomethyl mercury (II) compounds (discussed in Section 6.2.1) are not volatile due to low vapor pressures, low Henry's Law coefficients and water solubility. As a conservative determination, Section 6.2.3 calculates the methyl mercury (II) vapor concentration in evaporator conditions, which bound waste tank conditions.

As shown, elemental and dimethyl mercury are the only two volatile species of mercury. Therefore, monomethyl mercury complexes do not pose a vapor space flammability concern because they are not volatile.

6.2.1 Monomethyl Mercury (II) Cation

Monomethyl mercury (II), also referred to as methylmercury, is an organometallic mercuric cation and has a strong affinity for halogen anions (Cl^-, F^-, Br^-, or I^-), hydroxide (OH^-), sulfates (SO_4^{2-}) or nitrates (NO_3^-) [Ref. 8.5 & 8.10][2]. Therefore, in the alkaline conditions it will behave as a salt (minimal vapor pressure) and its concentration in the vapor space will be limited to liquid entrainment (See Figure 6-2) [Ref. 8.12]. The halogen content of the waste is closely monitored and controlled under the WAC due to the potential for aggressive attack on the carbon steel waste tanks. Consequently, the halogen concentrations are very low and not likely to contribute to a measurable vapor presence [Ref. 8.7]. Of the halogens, chloride is likely to have the highest concentration in the supernate (See Figure 6-3). If CH_3HgCl is generated, its vapor pressure is low (See Table 6-1) [Ref. 8.8][3]. Thus, the likely forms that the monomethyl mercury cation would make, due to the availability of nitrates and hydroxides, are $CH_3Hg + NO_3^-$ and/or $CH_3Hg + OH^-$(See Table 6-2 indicating that these compounds are non-reactive). However, the most likely form of methyl mercury for highly alkaline High Level Waste (HLW) will be CH_3HgOH [Ref. 8.36]. Studies have shown that the methyl mercury cation is subject to hydration in an aqueous environment forming hydroxides or various oxoniums[4], depending on pH [Ref. 8.6]. Therefore, once the ion CH_3Hg^+ is hydrated it could yield four nonvolatile derivatives of methyl mercuric hydroxide (See Appendix 9.2). The reaction of methyl mercury to form nitrated forms occurs principally with nitric acid; nitrate can also cause decomposition of methyl mercury to mercuric ion (Hg^{2+}). In mercury laboratory sample analyses, acid is used to stabilize volatile mercury compounds [Ref. 8.9]. This suggests that a reaction with nitrates in an aqueous environment to form volatile compounds will not occur. The Hg-N linkage in organic compounds that have been studied are the mercury compounds of the acid amides and imides. These substances dissolve mercuric oxide readily producing Hg-N compounds. These compounds will behave as mercuric salts except they will not react readily with bases [Ref. 8.28]. In addition, both hydroxide and nitrate methyl mercury salts are less volatile and less hazardous than short-chain alkylmercuric compounds [Ref. 8.27 & 8.29]. Based on the available anions in SRS waste, methyl mercuric hydroxide and nitrate will be the most probable species of methyl mercury present. As shown in Table 6-1, methyl mercuric hydroxide has the highest vapor pressure and lowest melting point out of all methyl mercuric species. Methyl mercuric nitrate is stable, water soluble and does not readily react with bases. Although methyl mercury compounds are classified as organo-metallic compound, due to the inability to get into the vapor phase, they do not contribute to the lower flammability limit.

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[2] CH_3Hg^+ can exist free only in minute concentrations; the affinity of CH_3Hg^+ for some ligands is high, especially toward thiol group [Ref. 8.13].

[3] Methyl mercuric chloride is not anticipated. The chloride content in the waste is carefully controlled because of corrosion concerns. If it does form, it will form a solid that settles to the sludge/solids layer in a waste tank (Specific gravity is 4.063 g/mL). It begins to transition to a liquid at 170° C. At 25°C, it has a vapor pressure of 8.5E-3 mmHg with a Henry's law coefficient is of 3.7E-7 atm-m^3/mol (1.51E-05, unitless) [Ref. 8.8]. Methyl mercuric fluoride, bromide (Melting point ~ 172°C), and iodide are mentioned above; however, they are not anticipated because of the very low levels of these anions in SRS waste.

[4] An oxonium ion is a species containing an oxygen atom that has an octet of valence electrons but has an overall formal charge of 1+ [Ref. 8.10].

Figure 6-2: Equilibrium Concentrations in air of some Mercury Compounds [Ref. 8.1]

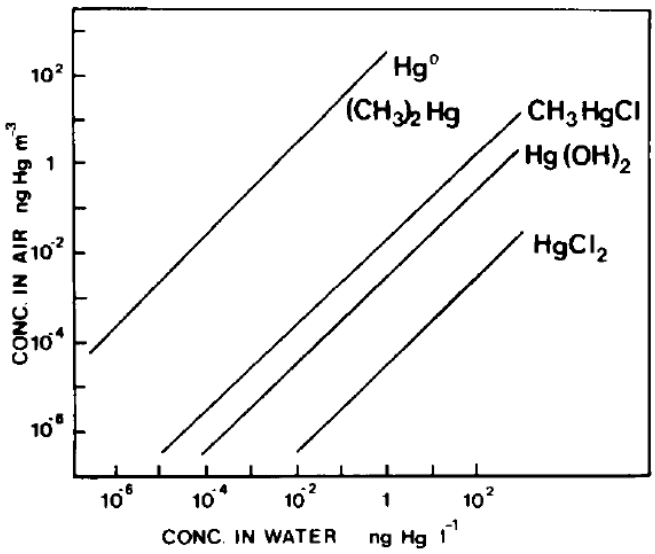
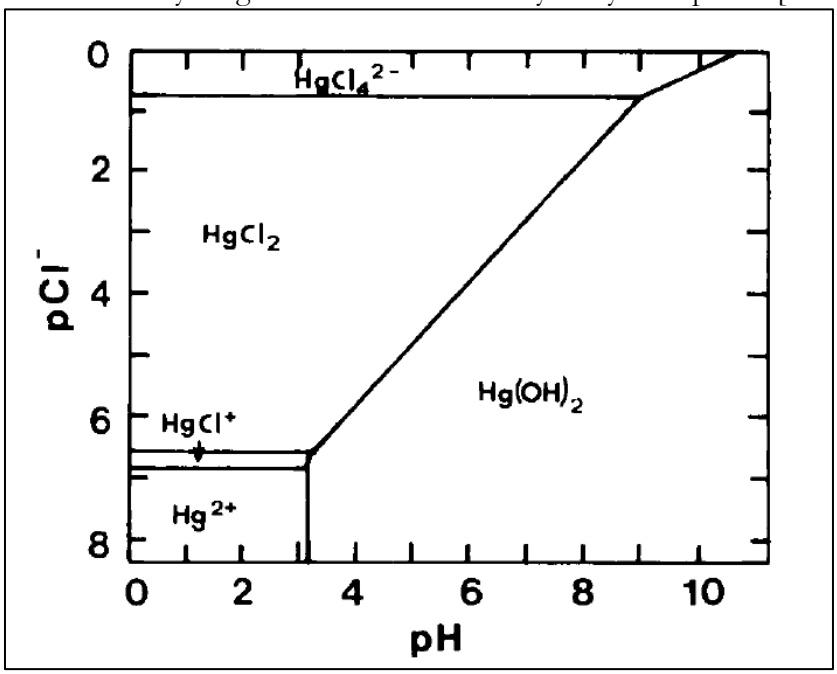


Fig. 3. Equilibrium concentrations in air of some mercury compounds as a function of corresponding concentrations in the water phase obtained from experimentally determined air/water constants at 25 °C (cf. Table 5). The curves for Hg^0 and $(CH_3)_2$ Hg coincide.

Figure 6-3: Stability ranges from Chloro- and Hydroxyl-complexes [Ref. 8.1]



Stability ranges from chloro- and hydroxyl-complexes of divalent mercury in aqueous solutions. The vertical axis represents the negative logarithm of the chloride concentration.

6.2.2 Dimethyl Mercury and Elemental Mercury

Some of the mercury bound in sludge or solution may be transformed to a volatile species that are emitted (or re-emitted) to the vapor phase. The two mercury species most likely to be released into the vapor space at the air/water interface, on the basis of their volatility, are elemental mercury and dimethyl mercury [Ref. 8.14]. Of the two substances, dimethyl mercury is the only flammable compound. It does not pose any serious fire or explosion hazard and is mildly endothermic[5]. Although it does not ignite in air, the compound is capable of burning quickly [Ref. 8.24]. Both elemental and dimethyl mercury are defined as volatile based on their relatively high air/water distribution constant (K_H), approximately 0.3 (See Table 6-1) and the Henry's Law relationship involving the ratio of vapor pressure to water solubility [Ref. 8.14]. The magnitude of the constant means that an air concentration of 1 ng/m^3 of either compound is in equilibrium with only 0.003 ng/L in the water phase, indicating the propensity for these forms of mercury to volatilize into the vapor space (See Figure 6-2). Which of the two compounds dominates the vaporization process is unknown, but studies have indicated that an appreciable amount of the dimethyl mercury that is emitted can have a relatively fast degradation to elemental mercury in air [Ref. 8.1 & 8.2].

The Lower Flammability Limit (LFL) is the lowest compound concentration in air that will support flame propagation. Due to dimethyl mercury's capabilities to volatilize, an LFL is necessary to establish an appropriate safety basis. Experimental data can be used to determine an LFL for laboratory tested species; however, the toxicity of dimethyl mercury has restricted laboratory analyses. Methodology has been developed to estimate the LFL of pure chemicals at a single temperature point. Table 6-3 shows four separate LFL determinations for dimethyl mercury. The most conservative case will bound the dimethyl mercury LFL volume percent.

Table 6-3: The LFL (volume %) for the Four Separate Cases

Dimethyl Mercury	**Case 1**	**Case 2**	**Case 3**	**Case 4**
Determined LFL (volume %)	2.9	14.6	3.04	2.5
Equation	4 & 5	4 & 5	6 & 7	-

The LFL as summarized in Cases 1-3 was determined using known correlations and approximations, and are discussed in detailed in Appendix 9.3. Case 1 and 2 assumed two different flash point temperatures to calculate the respective vapor pressure using Antoine coefficients [Ref. 8.15]. Case 3 used an equation developed by Catoire and Naudet to determine an empirically based prediction method for compounds containing carbon, hydrogen or oxygen atoms [Ref. 8.25].

Case 4 was determined assuming a theoretical impact of the moles of methane that are produced by each mole of dimethyl mercury, and conservatively assumes the worst impact of those moles on the LFL. When dimethyl mercury breaks down due to excessive heat or pressure, it yields a complex mixture of gases (i.e., methane, ethane, ethylene, etc.). Case 4 assumes as soon as dimethyl mercury is released into the vapor, it will decompose into 2 methanes and mercury. Dimethyl mercury LFL could be as much as half of methane's known LFL (5.0 volume %) because dimethyl mercury produces 2 moles of methane per 1 mole of dimethyl mercury. Thus, for conservatism, the LFL for

[5] All reactive hazards involve the release of energy in quantities or at rates too high to be absorbed by the immediate environment of the reacting system. The source of the energy may be an exothermic multicomponent reaction, or the exothermic decomposition of a single unstable (often endothermic) compound [Ref. 8.32].

methane is reduced by the number of methanes that in theory could be released as a by-product of dimethyl mercury. Of the LFL results shown in Table 6-3, Case 4 was determined to be a reasonably bounding LFL for dimethyl mercury. Bounding the LFL helps account for the unidentified organo-metallic material. In addition, other dimethyl species have been found to have an LFL in the range of 1.4-3.4 (2, 2-dimethylpropane – dimethyl Ether) [Ref. 8.26]. Based on the results of Case 1 and 3, and after comparing the chemical composition of dimethyl mercury to other similar compounds, it is determined that this LFL bounds the actual LFL of dimethyl mercury.

6.2.3 Concentration of Methyl Mercury (II) Compounds in the Evaporator Vapor Space

To show the minimal impact of methyl mercury (II) compounds in the vapor space of process locations within the Liquid Waste system, the evaporator conditions were chosen for illustration since the evaporator operates at conditions exceeding boiling point temperatures of some mercury complexes. Equations 1 and 2 below calculate a mercury vapor concentration in the evaporator. The vapor pressure is relatively low in the evaporator vapor space and sufficient material may be available to establish equilibrium and solubilize methyl mercury compounds. Consequently, methyl mercuric hydroxide was selected not only because it is the most likely species found in SRS waste, but also to illustrate the minimal impact of methyl compounds on the vapor space. Using 2 sigma on the reported data from Eurofins speciation analysis (See Section 6.3, [Ref. 8.19][6]), the methyl mercury liquid concentration is 95.23 mg/L. Equation 1 determines what the vapor concentration would be if methyl mercuric hydroxide was fed to the evaporator.

$$H = \frac{C_v}{C_l} \; or \; C_v = H * C_l$$

[Equation 1]

Where,
Henry's Law Coefficient, H= 5.48E-9 unitless, (See Table 6-1)
Liquid Concentration, C_l= 95.23 mg/L, [Ref. 8.19]
Vapor Concentration, C_v= 5.22 E-7 mg/L or 5.22E-4 mg/m^3 in the vapor space

Converting the vapor concentration as a volume percent:

$$volume\ \% = \frac{5.22E^{-7} mg}{L} * \frac{1g}{10^3 mg} * \frac{1\ mol}{232.63\ g} * \frac{22.4\ L}{1\ mol} * \frac{459.15K}{273.15K} * 100 = 8.45E^{-9}\ volume\ \%$$

[Equation 2]

Where,
Operating Temperature = 186°C + 273.15K = 459.15K
Reference Temperature = 273.15K
Gas Constant = 22.4 L/mol

The high solubility and low Henry's Law coefficient restrict the level of monomethyl mercuric hydroxide reaching and condensing in the vapor space. By making a very conservative assumption that the monomethyl mercuric hydroxide concentration in the feed to the evaporator is 1,000 times

[6] The reported data from Eurofins speciation analysis for methyl mercury was 53.5mg/L with a RSD of 39%. In order to conservatively estimate the 2 sigma uncertainty applied to the analysis result of 53.5mg/L, 39% of the concentration must be determined, doubled and added to the total methyl mercury value. $\frac{53.5\ mg}{L} * \frac{39\%}{100\%} = 20.865 \frac{mg}{L} * 2 = 41.73 \frac{mg}{L} + 53.5 \frac{mg}{L} = 95.23 \frac{mg}{L}$

greater, the vapor concentration is still negligible, 5.22E-1 mg/m^3, 8.45E-6 volume %, at 186°C. Note that this is not intended to be a flammability evaluation for the evaporator but only serves to demonstrate low methyl mercury compound vapor concentrations even in evaporator conditions. Lower temperature conditions associated with other portions of the Liquid Waste system (See Assumption 5.2) would result in even lower vapor space concentrations.

6.3 Tank 50 Eurofins Sample Analysis [Ref. 8.19]

6.3.1 Background

Historically, Eurofins Frontier Global Sciences, Inc. has provided mercury speciation analysis for SRS waste and has been viewed as a reputable mercury analysis laboratory. Eurofins' mercury analysis can only determine mercury speciation concentrations for the following; total Hg, total soluble Hg, particulate Hg, elemental Hg, ionic Hg, methyl Hg, ethyl Hg, and dimethyl Hg. In the sample preparation process, the samples are preserved in order to ensure a mercury concentration representative of SRS waste.

Two Tank 50 samples were collected and sent to Eurofins for mercury speciation analysis (1QCY15 and 2QCY15) [Ref. 8.19 & 8.22]. Both 1QCY15 and 2QCY15 samples are variable depth Tank 50 WAC Slurry Samples and collected at 35" and 66" from the bottom of the tank, respectively. Although these samples were pulled at two separate depths, they are both considered to be representative of Tank 50 because they are slurry samples (the tank was mixed prior to collection of the sample) [Ref. 8.37]. A summary of the results (in mg/L) from the analysis of these two samples is shown in Table 6-4.

Table 6-4: Eurofins Mercury Speciation Data (mg/L) [Ref. 8.19 & 8.22]

Sample Pull Date	**Sample**	**Total Hg**	**Total Soluble Hg**	**Particulate Hg**	**Elemental Hg** [Hg^0]	**Ionic Hg** [Hg^{1+} & Hg^{2+}]	**Methyl Hg**	**Ethyl Hg**	**Dimethyl Hg**	**Species Fraction of Total Hg**
February 25, 2015	**1QCY15**	126	ND	ND	0.912	5.04	53.5	ND	0.00219	47%
	1QCY15 (with %RSD added)	138.6	ND	ND	0.108	5.65	74.77	ND	0.00245	ND
April 7, 2015	**2QCY15**	97.7	94.3	3.4	1.04	4.86	53.0	14.2	0.0235	78%
	2QCY15 (with %RSD added)	102.6	102.7	No % RSD	1.21	6.03	54.54	15.28	0.0266	ND

*ND: Not Determined

Table 6-4 proposes two discussions on the accuracy of the replicate samples and methyl mercury to ethyl mercury ratio. Due to the complexity of mercury speciation analysis, the data Eurofins provided contains varied %RSD (Relative Standard Deviation) values. Table 6-4 provides the Eurofins reported sample data with the %RSD applied to the appropriate species. The 2QCY15 sample analysis validates that the methyl mercury concentration is larger than the ethyl mercury concentration.

6.3.2 Unidentified Mercury Speciation

Studies have shown that one of the dominant processes controlling mercury compound distribution is sorption of nonvolatile forms on particulates [Ref. 8.6]. Therefore, through the filtration of samples, some of the methyl mercury compounds are adsorbed onto the particulates and filtered out. Based on the aforementioned information, it is possible that the unidentified mercury speciation in the Tank 50 Eurofins sample is methyl mercury compounds that adsorbed onto the particles present in the sample [Ref. 8.19].

Available Hg(II) present in the waste would undergo the alkylation[7] process to form an organomercury compound. The formation of organic radicals is dependent on the available hydrocarbon species in waste. Stability of alkyl groups increases in the order methyl < ethyl < propyl < butyl [Ref. 8.31]. The longer chain alkyl groups are more stable than the methyl group. Thus, the abundance of the alkyl groups in waste would be inverse to stability, methyl > ethyl > propyl > butyl. This would indicate that more dominant functional groups present in the SRS waste are methane and ethane because they are the most reactive and the least stable and can readily alkylate Hg(II) to form a methyl/ethyl mercury cation.

Although they are not expected to be as abundant as methyl and ethyl, propyl and butyl groups from existent carbon chains could dissociate to form mercury complexes in SRS waste. As stated in Section 6.2, the hydrocarbon mercury compound properties are dependent upon the nature of the inorganic radical or anion. These organic mercury compounds will behave similarly to methyl mercury as a covalent substance or an ionic salt-like compound.

In the case that the unidentified mercury species is another compound and not a methyl mercury (II) compound, it can be assumed to be bounded by dimethyl mercury, which was analyzed during sample analysis [Ref. 8.19 & 8.22]. As addressed in Assumptions 5.4 and 5.5, dimethyl mercury is considered to be the most abundant dialkyl species. Thus, the dimethyl mercury concentration is the most bounding flammable concentration.

7 Conclusion

The projected organomercury (II) complexes found in waste tanks under normal operating conditions were evaluated to assess their chemical characteristics with respect to volatility and flammability. It is anticipated that most of the mercury will be present as methyl mercury compounds (e.g., methyl mercuric hydroxide, methyl mercuric nitrate, etc.). The likely methyl mercury species will act as a salt and is categorized as a solid. Methyl mercury compounds are not volatile due to low vapor pressures, low Henry's Law coefficients and water solubility. Even in conditions exceeding its established boiling point (e.g., when exposed to elevated temperatures as seen during evaporator operations), methyl mercury was determined to have a negligible vapor concentration. This bounds the conditions observed during normal waste tank and Saltstone operations.

The mercury species that have been identified as volatile are elemental mercury and dialkyl mercury. Both elemental and dimethyl mercury were identified during speciation sample analysis, and were

[7] Alkylation is the transfer of an alkyl group from one molecule to another [Ref. 8.28].

determined to have considerably lower concentrations than monomethyl mercuric compounds. Of these substances, dimethyl mercury is the only compound of flammability concern with a conservatively calculated LFL of 2.5 volume %. The remaining mercury species that were not identified in the sample analysis could be a mono-methyl or mono-ethyl mercury complex or dialkyl mercury species. As discussed above, the likely forms or complexes of monomethyl mercury are not volatile or flammable, thus are not a flammability concern. In the event the complexes have larger alkyl groups, their impact on flammability is bound by dimethyl mercury because other known complexes (e.g., diethyl mercury, dipropyl mercury, dibutyl mercury, etc.) do not readily form due to their stability, and their concentrations would be expected to be smaller. Dimethyl mercury has been identified to be the most abundant and volatile dialkyl species; the dimethyl mercury flammability bounds that of larger dialkyl species.

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9 Appendix

9.1 Additional Mercury Compounds Evaluated

The compounds listed in Table 9-1 were discounted as probable species in the Tank 50 waste stream because of temperature, complex formation, ion availability, pH, chemical kinetics and thermodynamics. As discussed in Section 6.3.2, the kinetic formation of mercury compounds favor methyl and ethyl complexes. Historically, sample analyses have been performed to identify and develop impacts of organics on the Tank Farm, described in Reference 8.23. The purpose of the compounds listed in Table 9-1 is to identify additional mercury species dismissed for further mercury discussion.

Table 9-1: Additional Mercury Compounds

Substance Name	Molecular Formula
(2,5-dichloro-3,6-dihydroxy-p-benzoquinolato)mercury	$C_6Cl_2HgO_4$
(5-(hydroxymercuri)-2-thienyl)mercury acetate	$C_6H_6Hg_2O_3S$
(acetato)(2,3,5,6-tetramethylphenyl)mercury	$C_{12}H_{16}HgO_2$
(acetato)(diethoxyphosphinyl)mercury	$C_6H_{13}HgO_5P$
acetoxy(2-acetamido-5-nitrophenyl)mercury	$C_{10}H_{10}HgN_2O_5$
bis(3-hydroxy-1-propynyl)mercury	$C_6H_6HgO_2$
bis(4-methylphenyl)mercury	$C_{14}H_{14}Hg$
bis(4-morpholinecarbodithioato)mercury	$C_{10}H_{16}HgN_2O_2S_4$
bis(cyclopentadienylchromium tricarbonyl)mercury	$C_{16}H_{10}Cr_2HgO_6$
bis(diethyldithiocarbamato)mercury	$C_{10}H_{20}HgN_2S_4$
bis(dimethylarsinyldiazomethyl)mercury	$C_6H_{12}As_2HgN_4$
bis(ethoxycarbonyldiazomethyl)mercury	$C_8H_{10}HgN_4O_4$
bis(formylmethyl) mercury	$C_4H_6HgO_2$
bis(trimethylsilyl)mercury	$C_6H_{18}HgSi_2$
chloro((3-(2,4-dioxo-5-imidazolidinyl)-2-methoxy)propyl) mercury	$C_7H_{11}ClHgN_2O_3$
chloro(2-(3-methoxypropionamido)cyclohexyl)mercury	$C_{10}H_{18}ClHgNO_2$
chloro(2-chlorovinyl)mercury	$C_2H_2Cl_2Hg$
chloro(2-furyl)mercury	C_4H_3ClHgO
chloro(2-hydroxy-3,5-dinitrophenyl)mercury	$C_6H_3ClHgN_2O_5$
chloro(dibutoxyphosphinyl)mercury	$C_8H_{18}ClHgO_3P$
chloro(diisopropoxyphosphinyl)mercury	$C_6H_{14}ClHgO_3P$
chloro(trans-2-methoxycyclooctyl)mercury	$C_9H_{17}ClHgO$
chloromethyl mercury	CH_3ClHg
copper (I) mercury iodide	Cu_2HgI_4
di-(bistrifluoromethylphosfido)mercury	$C_4F_{12}HgP_2$
diethyl mercury	$C_4H_{10}Hg$
iodo(p-tolyl)mercury	C_7H_7HgI
mercuric acetate, 4-aminophenyl	$HgC_8H_9NO_2$
mercuric acetate, phenyl	$HgC_8H_8O_2$

Substance Name	Molecular Formula
mercuric bromide	$HgBr_2$
mercuric chloride, phenyl	HgC_6H_5Cl
mercuric iodide	HgI_2
mercuric potassium cyanide	$C_4HgK_2N_4$
mercury (I) acetate	$Hg_2C_4H_6O_4$
mercury (I) bromide	Hg_2Br_2
mercury (I) carbonate	Hg_2CO_3
mercury (I) chlorate	$Hg_2Cl_2O_6$
mercury (I) chloride	Hg_2Cl_2
mercury (I) chromate	Hg_2CrO_4
mercury (I) fluoride	Hg_2F_2
mercury (I) iodate	$Hg_2I_2O_6$
mercury (I) iodide	Hg_2I_2
mercury (I) nitrate dihydrate	HgH_4NO_5
mercury (I) nitrate dihydrate	$Hg_2H_4N_2O_8$
mercury (I) nitrate monohydrate	HgH_2NO_4
mercury (I) oxide	Hg_2O
mercury (I) perchlorate tetrahydrate	$HgClH_8O_8$
mercury (I) sulfate	Hg_2SO_4
mercury (I) sulfide	Hg_2S
mercury (II) acetate	$HgC_4H_6O_4$
mercury (II) amide chloride	$HgClH_2N$
mercury (II) benzoate monohydrate	$HgC_{14}H_{12}O_5$
mercury (II) bromide, phenyl	HgC_6H_5Br
mercury (II) chromate	$HgCrO_4$
mercury (II) cyanide	HgC_2N_2
mercury (II) dichromate	$HgCr_2O_7$
mercury (II) fluoride	HgF_2
mercury (II) fulminate	$HgC_2N_2O_2$
mercury (II) hydride	HgH_2
mercury (II) hydrogen arsenate	$HgHAsO_4$
mercury (II) iodate	HgI_2O_6
mercury (II) nitrate	HgN_2O_6
mercury (II) nitrate dihydrate	$HgH_4N_2O_8$
mercury (II) nitrate hemihydrate	$HgHN_2O_{6.5}$
mercury (II) nitrate monohydrate	$HgH_2N_2O_7$
mercury (II) oleate	$HgC_{36}H_{66}O_4$
mercury (II) oxalate	HgC_2O_4
mercury (II) oxide	HgO
mercury (II) oxycyanide	$Hg_2C_2N_2O$

Substance Name	Molecular Formula
mercury (II) perchlorate trihydrate	$HgCl_2H_6O_{11}$
mercury (II) phosphate	$Hg_3O_8P_2$
mercury (II) selenide	HgSe
mercury (II) sulfate	$HgSO_4$
mercury (II) sulfide (black)	HgS
mercury (II) sulfide (red)	HgS
mercury (II) sulfide(α)	HgS
mercury (II) sulfide(β)	HgS
mercury (II) telluride	HgTe
mercury (II) tetrathiocyanatocobaltate (II)	$HgC_4CoN_4S_4$
mercury (II) thiocyanate	$HgC_2N_2S_2$
mercury (II) trifluoroacetate	$HgC_4F_6O_4$
mercury (II) trifluoromethanesulfonate	$HgC_2F_6O_6S_2$
mercury acetylide (DOT)	C_2HHg
mercury bis(chloroacetylide)	C_4Cl_2Hg
mercury gluconate	$C_6H_{11}HgO_7$
mercury salicylate	$C_7H_4HgO_3$
mercury thiocyanatocobaltate(II)	$C_4CoHgN_4S_4$
mercury(I) acetate	$C_4H_6Hg_2O_4$
mercury(I) cyanamide	CHg_2N_2
mercury(II) 5-nitrotetrazolide	$C_2HgN_{10}O_4$
mercury(II) acetate	$C_4H_6HgO_4$
mercury(II) acetylide	C_2Hg
mercury(II) aci-dinitromethanide	$C_2H_2HgN_4O_8$
mercury(II) cyanate	$C_2HgN_2O_2$
mercury(II) cyanide	C_2HgN_2
mercury(II) edta complex	$C_{10}H_{14}HgN_2O_8$
mercury(II) formohydroxamate	$C_2H_4HgN_2O_4$
mercury(II) fulminate	$C_2HgN_2O_2$
mercury(II) methylnitrolate	$C_2H_2HgN_4O_6$
mercury(II) oxalate	C_2HgO_4
mercury(II) phenyl acetate	$C_8H_8HgO_2$
mercury(II) thiocyanate	$C_2HgN_2S_2$
mercury, bis (trimethylsilylmethyl)	$HgC_8H_{22}Si_2$
mercury, diphenyl	$HgC_{12}H_{10}$
mercury-2-naphthalenediazonium trichloride	$C_{10}H_7Cl_3HgN_2$
mercury-O,O-di-n-butyl phosphorodithioate	$C_{16}H_{36}HgO_4P_2S_4$
methyl(5-isopropyl-N-(p-tolyl)-o-toluenesulfonamido)mercury	$C_{18}H_{23}HgNO_2S$
methyl(methylthio)mercury	C_2H_6HgS
methyl(thioacetamido) mercury	C_3H_7HgNS

Substance Name	Molecular Formula
methyl-mercury toluenesulphamide	$C_9H_{14}Hg_2N_2O_2S$
N-bis(p-tolylsulfonyl)amidomethyl mercury	$C_{15}H_{17}HgNO_4S_2$
o-nitrophenyl mercury acetate	$C_8H_7HgNO_4$
phenyl mercury nitrate, basic	$Hg_2C_{12}H_{11}NO_4$
trans-chloro(2-(3-bromopropionamido)cyclohexyl)mercury	$C_9H_{15}BrClHgNO$
trans-chloro(2-hexanamidocyclohexyl)mercury	$C_{12}H_{22}ClHgNO$

9.2 Methyl Mercuric Hydroxide Reaction [Ref. 8.12]

The three reactions below show that in high nitrate and pH solutions it is possible to yield four derivatives of methyl mercuric hydroxide species in solution (derivative species are in bold). Due to the nature of SRS waste, it is possible any four of these species to exist. The ion CH_3Hg^+ is hydrated in aqueous solution and the pH dependency leads to the formation of oxonium ions.

1. $\mathbf{CH_3Hg(OH_2)^+} + OH^- \leftrightarrow \mathbf{CH_3HgOH} + H_2O$

2. $CH_3Hg(OH_2)^+ + CH_3HgOH \leftrightarrow \mathbf{(CH_3Hg)_2OH^+} + H_2O$

3. $CH_3HgOH + (CH_3Hg)_2OH^+ \leftrightarrow \mathbf{(CH_3Hg)_3O^+} + H_2O$

The resulting hydrated species, $CH_3Hg(OH_2)^+$ is also a cation and in high caustic solutions can result in CH_3HgOH, and pH dimers and trimers; $(CH_3Hg)_2OH^+$ and $(CH_3Hg)_3O^+$. These species are also ionic with limited to negligible volatility and would pose no vapor space flammability concern.

9.3 Dimethyl Mercury LFL Calculation Methodology

Table 9-2: Case 1 and 2 Methodology Inputs [Ref. 8.15 & 8.24]

Dimethyl Mercury (Using Antoine Coefficients)	**Case 1**	**Case 2**
Flash Point (°C) – Established	5	38
Equations Used	4	4
Vapor Pressure at Flash Point (mmHg)	22.66	111.12

$$P = 10^{\left[A - \frac{B}{C+T}\right]}$$

[Equation 3]

Where,
P= Vapor pressure, mmHg, (See Table below)
Antoine Coefficients [Ref.8.15];
A= 6.91434
B= 1293.43
C= 227.67
T= Temperature specified in Table 9-3

Table 9-3: Determined Vapor Pressure using Equation 3

Temperature (°C)	**Vapor Pressure (mmHg)**
0	17.10719
5	**22.66026**
10	29.66295
15	38.40118
20	49.19798
25	62.41535
30	78.45576
35	97.76347
38	**111.1172**
40	120.8255
45	148.1724
50	180.3784

$$y_{DMHg} = \frac{P_{vp}}{P} * 100\%$$

[Equation 4]

Where,
[Case 1] y_{DMHg} = Volume percent of DMHg in the vapor space, 2.98 vol% (Calculated in Equation 4)
P_{vp} = Vapor pressure of DMHg at 5°C, 22.66 mmHg (Calculated in Equation 3)
P = System pressure, 760 mmHg

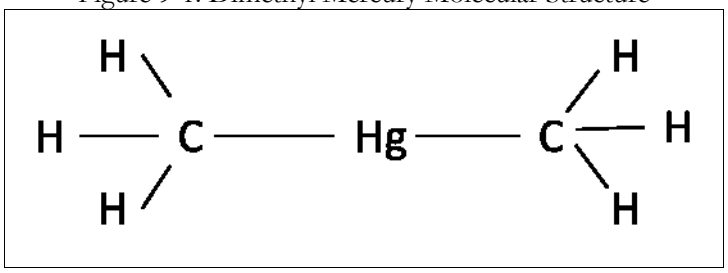
[Case 2] y_{DMHg} = Volume percent of DMHg in the vapor space, 14.62 vol% (Calculated in Equation 4)
P_{vp} = Vapor pressure of DMHg at 38°C, 111.12mmHg (Calculated in Equation 3)
P = System pressure, 760 mmHg

Case 1 and 2 were determined using Antoine equations and coefficients to determine vapor pressure at designated temperatures. Using the vapor pressure at each flash point temperature, Case 1 and 2 were determined to have an LFL of 2.9% and 14.6%, respectively.

Table 9-4: Case 3 Methodology Inputs [Ref. 8.25]

Dimethyl Mercury (Using Catoire and Naudet)	**Case 3**
Temperature (°C)	25
Number of Carbons (n_c), See Figure 9-1	2
Number of Hydrogens (n_H), See Figure 9-1	6
Number of Oxygens (n_O), See Figure 9-1	0

Figure 9-1: Dimethyl Mercury Molecular Structure



$$LFL(T) = 519.957 * X^{0.71936} * {n_C}^{-0.197} * T^{-0.51536}$$

[Equation 5]

Where,
LFL(T) = LFL at 25°C or 298.15K, 3.04 vol % (Calculated)
n_c= Number of carbons in DMHg, 2 (See Figure below)
T= 298.15K

$$X = \frac{1}{1 + 5n_C + {}^{5}/_{4n_H} - {}^{5}/_{2n_O}}$$

[Equation 6]

Where,
n_c= Number of carbons in DMHg, 2 (See Table 9-4)
n_H= Number of hydrogens in DMHg, 6 (See Table 9-4)
n_O= Number of oxygen in DMHg, 0 (See Table 9-4)
X = 0.054 (Calculated in Equation 6)

Case 3 was determined using an equation developed by Catoire and Naudet to determine an empirically based prediction method for compounds containing carbon, hydrogen or oxygen atoms [Ref. 8.25]. Equation 5 establishes an LFL for dimethyl mercury of 3.04 volume %.

9.4 Additional Dialkyl Mercury LFL Calculation Methodology

Due to the lack of Antoine coefficient data for these substances, the LFL was only determined using only Cases 3 and 4.

Table 9-5: Case 3 Methodology Inputs [Ref. 8.25]

Dialkyl Mercury	Diethyl	Dipropyl	Dibutyl
Temperature (°C)	25	25	25
Number of Carbons (n_c), See Figure 9-1	4	6	8
Number of Hydrogens (n_H), See Figure 9-1	10	14	18
Number of Oxygens (n_O), See Figure 9-1	0	0	0

Case 3 was determined using Equations 5 and 6, in Section 9.3, to determine an empirically based prediction method for compounds containing carbon, hydrogen or oxygen atoms [Ref. 8.25]. Table 9-8 reports the LFL results for both Case 3 and 4.

Table 9-6: Methanes Produced from Dialkyl Decomposition for Case 4

Dialkyl Mercury	Diethyl	Dipropyl	Dibutyl
Methanes Yielded	4	6	8

Case 4 was determined assuming a theoretical impact of the moles of methane that are produced by each mole of the dialkyl mercury species, and conservatively assumes the worst impact of those moles on the LFL. Case 4 assumes as soon as the dialkyl mercury species is released into the vapor, it will decompose into methanes and mercury. Of the LFL results shown in Table 9-8, Case 4 was determined to be a reasonably bounding LFL for all dialkyl mercury species. In addition, Table 9-7 reports other dialkyl species LFL range. Based on the results of Case 3, and after comparing the chemical composition of dialkyl mercury to other similar compounds, it is determined that Case 4 LFL bounds the actual LFL of dialkyl mercury.

Table 9-7: Additional Dialkyl LFL Information [Ref. 8.26 & 8.35]

Species	LFL Range
Diethyl Ether-Diethyl peroxide	1.8 – 2.3
Diisopropyl Ketone	1
Disobutul Ketone	1

Table 9-8: The LFL (volume %) using Cases 3 and 4

Dialkyl Mercury LFL (Calculated)	Diethyl	Dipropyl	Dibutyl
Case 3	1.74	1.23	0.97
Case 4	1.25	0.83	0.63

10 Distribution

C.J. Bannochie
D.J. Blake
M.N. Borders
H.P. Boyd
J.M. Bricker
T.E. Britt
D.L. Burnfield
J.S. Contardi
C.D. Cope
W.J. Copeland
R.E. Edwards
T.L. Fellinger
J.K. Fortenberry
E.J. Freed
A.G. Hansen
P.J. Hill
T.H. Huff
J.F. Iaukea
V. Jain
M.T. Keefer
J.T. Knight
J.N. Leita
S.L. Marra
C.J. Martino
G.J. Matis
R.T. McNew
J.E. Occhipinti
F.M. Pennebaker
M.M. Potvin
J.W. Ray
M.T. Sautman
A.R. Shafer
H.B. Shah
C.B. Sherburne
P.C. Suggs
T.C. Temple
J.R. Vitali
W.R. Wilmarth