HNF-29785
Revision 0

Action Concentration for Mixtures of VOCs, Methane and Hydrogen

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-96RL13200

FLUOR.

P.O. Box 1000
Richland, Washington

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HNF-29785
Revision 0
EDC #: HNF-EDC-06-29902

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Fluor Government Group

Date Published
July 2006

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Total Pages: 22

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Action Concentration for Mixtures of VOCs, Methane and Hydrogen**1.0 INTRODUCTION**

Waste containers may contain volatile organic compounds (VOCs), methane, hydrogen and possibly propane. These constituents may occur individually or in mixtures. Determining if a waste container contains a flammable concentration of flammable gases and vapors (from VOCs) is important to the safety of the handling, repackaging and shipping activities. This report provides the basis for determining the flammability of mixtures of flammable gases and vapors. The concentration of a mixture that is at the lowest flammability limit for that mixture is called the action concentration. The action concentration can be determined using total VOC concentrations or actual concentration of each individual VOC. The concentrations of hydrogen and methane are included with the total VOC or individual VOC concentration to determine the action concentration. Concentrations below this point are not flammable. Waste containers with gas/vapor concentrations at or above the action concentration are considered flammable.

Sampling

The waste containers of interest are retrieved from the trench of interest and moved to a location where the headspace is sampled. The concentration of hydrogen, methane and total VOCs are obtained from the sample. "Total VOCs" are obtained using a gas chromatograph calibrated with propane to initially screen the container for its total flammable VOC content. HNF-29820, *Technical Justification for Choosing Propane as a Calibration Agent for Total Flammable Volatile Organic Compound Determinations* presents the justification of using propane as a calibration gas. If the VOC screen indicates a significant presence of flammable VOCs, then an additional sample can be taken and sent for laboratory identification and quantitation of the VOCs by gas chromatography – mass spectrometry (GC/MS).

Lower Flammability Limits

The lower flammability limit (LFL) for hydrogen and methane are well known and are 4% and 5% (volume percent in air), respectively.

The LFL for a sample analyzed only for "Total VOCs" is assigned a value of 10,000 ppm (or 1 vol%) based on the following. Table 1 of HNF-25634, *Potential for a Volatile Organic Compound (VOC) Deflagration in a TRU Drum* provides the LFL for all the VOCs identified to date at Hanford. These are reproduced in Table 1 below. Section 1.4 of the reference provides the basis for the list in HNF-25634. Of all the VOCs identified, only one has an LFL less than 1 vol%. That is trimethylbenzene. Its LFL is 0.9 vol%. It is interesting to note that only xylene and carbon disulfide have LFLs of 1 vol%. Only toluene, methyl isobutyl ketone, cyclohexane and chlorobenzene have an LFL between 1 vol% and 1.3 vol%. All the rest have LFLs above 1.3 vol% (a number of VOCs have LFLs between 1.4 vol% and 2 vol%).

The LFL for trimethylbenzene need not be considered because of the following. In practice, the identities of the VOCs in samples are not known; a propane-calibrated gas chromatograph is used only as a screening tool and does not identify the VOCs. However, if GC/MS analysis is

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required or desired to determine the species present, then correction factors are needed to determine the actual concentration of the VOCs present in the sample. The actual concentration present is defined by

$$\text{Actual concentration} = \text{measured concentration} * \text{CR}$$

where CR = correction factor.

The correction factors are taken from HNF-29820 and are shown in Table 1 below. The correction factor for trimethylbenzene is similar to that of benzene which is 0.33. (See HNF-29820 for a discussion of correction factors and Table 1 of this report for a reproduction of the data from HNF-29820). Therefore even if trimethylbenzene were the only constituent, a measured concentration of 1 vol% or 10,000 ppm would equate to about 4,000 ppm which is well below its LFL.

HNF-29820 also shows that the correction factors for isopropyl alcohol and methanol are above 1.0. Therefore if the only VOC present were one of these two VOCs, the actual concentration would exceed 1 vol% or 10,000 ppm. Table 1 of HNF-25634 shows that the LFL are

isopropyl alcohol	2%
methanol	7.3%

The correction factors (from HNF-29820 and shown in Table 1) are

isopropyl alcohol	1.5
methanol	1.4

Therefore even if the VOC concentration were 10,000 ppm and the only VOC present were isopropyl alcohol or methanol, the actual concentration would be 15,000 ppm or 14,000 ppm respectively. However, both concentrations are less than their respective LFL's.

From the above it is seen that it is conservative to set the LFL for "total VOC" at 1 vol% or 10,000 ppm.

2.0 FLAMMABILITY DETERMINATION OF A MIXTURE OF VOCS, METHANE AND HYDROGEN

Appendix 3.10 of the *CH-TRU Payload Appendices* provides the method by which the flammability limits are determined. The lower explosive limit (the term used in the reference which is the same as the lower flammability limit) for a single volatile organic gas or a mixture of gases is given by:

$$\text{MLEL} = \frac{100\%}{\sum_i f_i (\text{GCF})_i}$$

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where:

MLEL = mixture lower explosive limit (vol %)

f_i = fraction of gas "i" in the mixture of flammable gases (air and non-flammable VOCs are not included)

GCF_i = group contribution factor. The group contribution factors are either found in the reference or by noting that

$$LFL_i \text{ the lower flammability limit, fraction} = \frac{1}{GCF_i}$$

The Group Contribution Factors (GCF_i) are found in Table 3.10.5 of Appendix 3.10 of the *CH-TRU Payload Appendices*.

Using the definitions above, and using the LFLs used from Table 1 of HNF-25634, the mixture LFL can be found from:

$$\text{Mixture LFL, in percent} = \frac{1.0}{\sum_i \frac{f_i}{LFL_i}} \quad (1)$$

where LFL_i = lower flammability limit of VOC_i in percent (see Table 1).

If the sample of VOCs had been analyzed to obtain the individual VOCs present the weighted correction factor would be needed to obtain the actual concentration. The weighted correction factor for a mixture of VOCs in a sample may be calculated from

$$\text{Weighted correction factor} = \frac{1.0}{\sum_i \frac{f_i}{CF_i}} \quad (2)$$

where: f_i = volume fraction of component of all of the flammable VOC present (air and non-flammable VOCs not included)

CF_i = correction factor for component i (See Column 3 of Table 1).

In the examples analyzed below, the component specific data is:

Component	Correction Factor (Normalized to Propane) (from HNF-29820-See Table 1)	LFL, vol% (from HNF-25634)
Total VOC	1	1
acetone	0.78	2.6
Isopropyl alcohol	1.5	2
xylene	0.22	1
1,1,1-trichloroethane	0.56	6
methanol	1.4	7.3

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In the examples below, it is assumed that any sample of VOCs that has a measured concentration equal to or greater than 1 vol% or 10,000 ppm will be further analyzed, using GC/MS, to determine the identity and concentrations of the individual species. Example 4 presents a case where the total VOC is used.

2.1 EXAMPLE 1

Consider a mixture that contains a concentration of VOCs totaling 1.1 vol% (or 11,000 ppm) VOCs. Since the total VOC concentration exceeds 1 vol%, the sample is analyzed in detail to determine the species present, their concentration and the mixture LFL. After GC/MS analysis, it is found that the mixture is comprised of equal volumes of acetone and isopropyl alcohol. That is, 0.5 of each.

Using equation 2

$$\text{Weighted } CF = \frac{1}{\frac{0.5}{0.78} + \frac{0.5}{1.5}} = 1.026$$

The value of the weighted correction factor is in-between the two chemical-specific correction factors. The “actual” (corrected) concentration is

$$\text{Actual concentration} = 1.1 * 1.026 = 1.13 \text{ vol\% (or 11,300 ppm)}$$

Now consider the mixture LFL.

$$\text{Mixture LFL} = \frac{1}{\frac{0.5}{2.6} + \frac{0.5}{2.0}} = 2.26\% \text{ or } 22,600 \text{ ppm}$$

The actual concentration is half of the mixture LFL (from 1.13 vol% / 2.26 vol%).

2.2 EXAMPLE 2

Consider a gas sample that contains a concentration of VOCs totaling 1.4 vol% (14,000 ppm). Since the total VOC concentration exceeds 1 vol%, the sample is analyzed in detail to determine the species present, their concentration and the mixture LFL. After GC/MS analysis, it is found that the mixture is comprised of equal volumes of isopropyl alcohol and methanol. That is, 0.5 of each.

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Using equation 2

$$\text{Weighted CF} = \frac{1}{\frac{0.5}{1.5} + \frac{0.5}{1.4}} = 1.45$$

The weighted correction factor is in-between the two chemical-specific correction factors. The “actual” (corrected) concentration is

$$\text{Actual concentration} = 1.4 * 1.45 = 2.03 \text{ vol\% (or 20,300 ppm)}$$

Now consider the mixture LFL.

$$\text{Mixture LFL} = \frac{1}{\frac{0.5}{2} + \frac{0.5}{7.3}} = 3.14\% \text{ or } 31,400 \text{ ppm}$$

The mixture is 65% of the mixture LFL (from 2.03 vol% / 3.14 vol%).

2.3 EXAMPLE 3

Consider a gas sample that contains a concentration of VOCs totaling 2% (or 20,000 ppm). Since the total VOC concentration exceeds 1% (or 10,000 ppm), the sample is analyzed in detail to determine the species present, their concentration and the mixture LFL. After GC/MS analysis, it is found that the mixture is comprised of:

VOC	Concentration (As measured volume percent in headspace)	Frac of VOCs present	CF (from HNF- 29820 and Column 3 of Table 1)	LFL, vol% (from HNF-25634)
Acetone	0.2	0.1	0.78	2.6
Isopropyl alcohol	0.3	0.15	1.5	2
Xylene	0.4	0.2	0.22	1
Trichloroethane	0.6	0.3	0.56	6
methanol	0.5	0.25	1.4	7.3

First find the weighted mixture CF

$$\text{Weighted CF} = \frac{1}{\frac{0.1}{0.78} + \frac{0.15}{1.5} + \frac{0.2}{0.22} + \frac{0.3}{0.56} + \frac{0.25}{1.4}} = 0.54$$

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The actual concentration is $0.54 \times 2\% = 1.08 \text{ vol\%}$ or 10,800 ppm.

The mixture LFL is

$$\text{Mixture LFL, \%} = \frac{1}{\frac{0.1}{2.6} + \frac{0.15}{2} + \frac{0.2}{1} + \frac{0.3}{6} + \frac{0.25}{7.3}} = 2.5\% \text{ or } 25,000 \text{ ppm}$$

The actual VOC concentration is 43% of the VOC mixture LFL.

Now hydrogen and methane will be added to the mixture of VOC and the LFL of the VOC-hydrogen-methane mix will be determined.

Equation 1 will be used in this portion of the analysis. Equation 1 states:

$$\text{Mixture LFL, in percent} = \frac{1.0}{\sum_i \frac{f_i}{\text{LFL}_i}}$$

In this case,

$$f_{\text{voc}} = \frac{\text{Actual VOC Concentration}}{\text{Total Concentration}} \text{ for the VOC portion}$$

$$f_{\text{methane}} = \frac{\text{Methane Concentration}}{\text{Total Concentration}}$$

$$f_{\text{hydrogen}} = \frac{\text{Hydrogen Concentration}}{\text{Total Concentration}}$$

$$\text{Total Conc} = (\text{Actual VOC Concentration}) + (\text{Methane Concentration}) + (\text{Hydrogen Concentration})$$

The LFL for the VOCs is the mixture LFL.

Consider the mixture in example 3 plus 1% methane (LFL is 5%) and 2% hydrogen (LFL is 4%).

The actual concentration of VOCs is 1.08%. The VOC mixture LFL is 2.5 vol%. The total concentration of flammable gas constituents is:

$$1.08 \text{ vol\% VOC} + 1 \text{ vol\% methane} + 2 \text{ vol\% hydrogen} = 4.08 \text{ vol\%}$$

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In this case

$$\begin{aligned}f_{\text{voc}} &= 1.08/4.08 = 0.264 \\f_{\text{methane}} &= 1.0/4.08 = 0.245 \\f_{\text{hydrogen}} &= 2.0/4.08 = 0.490\end{aligned}$$

The mixture LFL is found from:

$$\text{Mixture LFL} = \frac{1}{\frac{0.264}{2.5} + \frac{0.245}{5} + \frac{0.490}{4}} = 3.61\% \text{ or } 36,100 \text{ ppm}$$

where the values of 2.5, 5 and 4 is the LFL for the VOC mixture, methane and hydrogen, respectively.

The mixture LFL = 3.61 vol% or 31,600 ppm.

The ratio of the total concentration to the mixture LFL = (4.08%) / (3.61%) = 1.13.

The mixture is 1.13 times the mixture LFL. The mixture is flammable.

2.4 EXAMPLE 4

Consider a gas sample that contains 9,000 ppm total VOCs plus 1% methane and 2% hydrogen. Since the VOC concentration is less than 1 vol%, the mixture does not have to be further analyzed to determine the species present. Flammability can be assessed using "Total VOC" concentration and an LFL of 1 vol%.

The total concentration of flammable gas constituents is:

$$0.9 \text{ vol\% VOC} + 1.0 \text{ vol\% methane} + 2.0 \text{ vol\% hydrogen} = 3.9 \text{ vol\%}$$

In this case,

$$\begin{aligned}f_{\text{voc}} &= 0.9/3.9 = 0.231 \\f_{\text{methane}} &= 1.0/3.9 = 0.256 \\f_{\text{hydrogen}} &= 2.0/3.9 = 0.513\end{aligned}$$

The mixture LFL is found from:

$$\text{Mixture LFL} = \frac{1}{\frac{0.231}{1.0} + \frac{0.256}{5} + \frac{0.513}{4}} = 2.44\% \text{ or } 24,400 \text{ ppm}$$

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where the values of 1.0, 5 and 4 is the LFL for the VOC mixture, methane and hydrogen, respectively.

The mixture LFL= 2.44 vol% or 24,400 ppm.

The ratio of the total concentration to the mixture LFL = 3.9 vol% / 2.44 vol% = 1.60.

The mixture is 1.6 times the mixture LFL. The mixture is flammable.

Assume the VOC are analyzed further to obtain the VOCs present. The table below presents the flammability of mixture of a particular VOC plus 1 vol% methane and 2 vol% hydrogen assuming that the entire measured concentration of 9,000 ppm is one of the VOC listed in column 1 of the table.

If the specific VOC present were (and its LFL is)	Correction Factor (from HNF-29820)	Actual Concentration of the VOC, ppm	Total Gas Conc., vol%	Volume Fractions • VOC • Methane • Hydrogen	Mixture LFL, vol%	Flammable or not (Col 4 vs. Col 6)
Acetone (2.6)	0.78	7020	3.7	0.19 0.27 0.54	3.8	No
Xylene (1.0)	0.22	1980	3.2	0.062 0.313 0.625	3.6	No
Isopropyl alcohol (2.0)	1.5	13,500	4.4	0.31 0.23 0.46	3.2	Yes
Butanol (1.4)	0.78	7020	3.7	0.19 0.27 0.54	3.1	Yes
Methyl ethyl ketone (1.8)	0.61	5490	3.55	0.155 0.28 0.56	3.55	Yes

2.5 DRUM MOVEMENT

Lastly, the Waste Retrieval Program (WRP) is allowed to move drums that have hydrogen concentrations below 15%. The argument is that should a deflagration occur, the drum would remain intact. If the VOCs are maintained below their effective LFL (a concentration less than

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1% for a sample analyzed as “Total VOCs”), and methane below its LFL, drum integrity is also maintained. From this a “drum movement” equation rather than an LFL equation can be developed.

The drums can be moved if

$$\frac{\%VOC}{1} + \frac{\%methane}{5} + \frac{\%hydrogen}{15} < 1.$$

3.0 INFORMATION NEEDED BEFORE USING THIS METHOD AS THE ONLY SCREENING METHOD

One of the limitations of the data in Table 1 is that the correction factors are valid only to 1000 ppmV. These correction factors are likely to vary at concentrations from 1000 ppmV to 10,000 ppmV. The variation is due to the fact that the detector response is non-linear at higher concentrations, and the extent of the non-linearity varies from compound to compound. Before the method presented above is used, the appropriate technical document (e.g., a revision to this document) needs to specify the measurement techniques, modified corrections factors or other means used to assure that a VOC measurement of less than 10,000 ppm is not, in fact greater than 10,000 ppm or the LFL of the vapor which ever is greater.

The methods above assume that, once the correction factor is applied, the concentration measured is the concentration that exists. That is, if 5000 ppm propane is measured, 5000 ppm of propane exists. To ensure confidence in the total flammable VOC numbers generated, a daily operational check must be run with a check standard, and criteria for passing the check must be established in the approved operating procedure.

An alternative approach that would satisfy the above two requirements and provide pertinent information is to, for some period of time, analyze those samples, that the screening tool shows VOC concentrations above 5,000 ppm (50% of the 10,000 limit), with the GC/MS and make the appropriate corrections to the correction factors, 10,000 ppm limit, and/or sample analysis procedure. This document should then be modified to include a discussion and justification of the changes. As data is obtained, the concentration at which samples should be analyzed by both methods can be increased, if warranted. The basis of using 5000 ppm is as follows. The right hand column of Table 1 shows the ratio of the actual gas concentration when the screening tool measures 5000 ppm, assuming that the actual correction factor at 5000 ppm is twice as large as it is between 50 and 100 ppm (See Note 2 of Table 1), to the LFL. While the actual increase in the correction factor between 100 ppm and 5000 ppm is not known, it is thought that it should not be greater than a factor of 2.

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The ratio is calculated by the following:

$$\text{Ratio} = \frac{\left(\frac{5000 \text{ ppm}}{1E6} \right) * (\text{Correction Factor } P) * 2}{\left(\frac{\text{LFL}}{100} \right)}$$

where: Correction Factor P = correction factor normalized to Propane (Column 3 in Table 1)

It will now be shown that even if the correction factors are twice as great at higher concentrations, the actual concentration is still below the LFL. Table 1 shows that the closest approach is isopropyl alcohol which has a ratio of 0.75. That means that even if the correction factor were off by a factor of 2 (a correction factor of 3 vs. 1.5), a concentration of 5000 ppm is still only 75% of its LFL. It should be noted that even with the increase in correction factor of a factor of two, most of the VOCs are still a quarter to a half of their LFL.

As stated above, as data is obtained, the concentration at which samples should be analyzed by both methods (set now at ≥ 5000 ppm) should be modified, if warranted.

4.0 REFERENCES

CH-TRU Payload Appendices, 2004, Waste Isolation Pilot Plant, Carlsbad, New Mexico.

HNF-25634, 2006, *Potential for a Volatile Organic Compound (VOC) Deflagration in a TRU Drum*, Rev. 0, Fluor Hanford, Inc., Richland, Washington.

HNF-29820, 2006, *Technical Justification for Choosing Propane as a Calibration Agent for Total Flammable Volatile Organic Compound Determinations*, Fluor Hanford, Inc., Richland, Washington.

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Table 1. Correction Factors and LFLs for Various VOCs

Flammable VOC	Correction Factor ²	Normalized to Propane ³	Lower Flammability Limit (Vol%) ⁴	Ratio (See Note 9)
acetone	1.4	0.78	2.6	0.30
benzene	0.6	0.33	1.4	0.24
butanol	1.4	0.78	1.4	0.56
carbon disulfide	0.44	0.24	1.0	0.24
chlorobenzene	0.39	0.22	1.3	0.17
chloroethane	1.1	0.61	3.6	0.17
cyclohexane	0.64	0.36	1.3	0.28
1,1-dichloroethane	< 0.89 ⁸	< 0.49	5.4	0.09
1,2-dichloroethane	0.6	0.33	6.2	0.05
1,2-dichloroethylene	0.34 ⁵	0.19	9.7	0.02
1,1-dichloroethylene	0.8	0.44	7.3	0.06
dichloromethane (methylene chloride)	0.89	0.49	15.5	0.03
dichloropropane	0.7 ⁶	0.39	3.4	0.11
dioxane	1.0 ⁸	0.6	2.0	0.30
ethyl benzene	0.51	0.28	1.6	0.18
ethyl ether (oxybisethane)	0.9 ⁸	0.5	1.9	0.26
isopropyl alcohol	2.7	1.5	2.0	0.75
methanol	2.5	1.4	7.3	0.19
methyl chloride (chloromethane)	0.74	0.41	8.1	0.05
methyl ethyl ketone	1.1	0.61	1.8	0.34
methyl isobutyl ketone	0.6	0.33	1.3	0.25
1,1,1-trichloroethane	1.0	0.56	6.0	0.09

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trichloroethylene	0.43	0.24	8.0	0.03
1,2,4-trimethylbenzene	0.3 ⁸	0.17	0.9	0.19
toluene	0.51	0.28	1.2	0.23
xylene	0.40 ⁷	0.22	1.0	0.22
propane	1.8	1.0	2.3	0.43
Other VOC				
carbon tetrachloride	1.7	0.94	Not flammable	

Notes:

¹ RAE Systems Inc. 2006.

² Correction factors are for an instrument calibrated with isobutylene. These correction factors were typically measured with the compound at 50 to 100 ppmV in dry air at room temperature. The correction factors may vary at concentrations greater than 1000 ppmV. RAE Systems Inc. (2006)

³ Computed by dividing the correction factor for each compound by the correction factor for propane.

⁴ From Table 1, Column 6 of HNF-25634, *Potential for a Volatile Organic compound (VOC) Deflagration in a TRU Drum*

⁵ Value is for trans-1,2-dichloroethylene.

⁶ Value is for 1,2-dichloropropane.

⁷ Value is the average of the correction factors for ortho-, meta-, and para-xylene.

⁸ Estimated values. See HNF-29820 for justification.

$$^9\text{Ratio} = \frac{\left(\frac{5000 \text{ ppm}}{1E6} \right) * (\text{Correction Factor } P) * 2}{\left(\frac{LFL}{100} \right)}$$

where: Correction Factor P = correction factor normalized to Propane
(Column 3 in this Table)

The term is the ratio of the actual gas concentration when the screening tool measures 5000 ppm, assuming that the actual correction factor at 5000 pm is twice as large as it is between 50 and 100 ppm (See Note 2), to the LFL. It is intended to show that even if the correction factors are twice as great at higher concentrations, the actual concentration is still below the LFL.

RAE Systems, Inc., 2006, *Correction Factors, Ionization Energies, and Calibration Characteristics*, Technical Note TN-106, Rev. 15,

http://www.raesystems.com/~raedocs/App_Tech_Notes/Tech_Notes/TN-106_Correction_Factors.pdf

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Desk Instruction 2.0, Rev. 1

CHECKLIST FOR TECHNICAL PEER REVIEWDocument Reviewed - HNF-29785 Rev. 0Title: Action Concentration for Mixtures of VOCs, Methane and HydrogenAuthor: R.M. MarusichDate: 5/17/2006 Scope of Review: Entire document

<u>Yes</u>	<u>No*</u>	<u>NA</u>	
☒	☐	☐	Referenced analyses appropriate.
☒	☐	☐	Problem completely defined and all potential configurations considered.
☐	☐	☒	Accident scenarios developed in a clear and logical manner.
☒	☐	☐	Necessary assumptions explicitly stated and supported.
☐	☐	☒	Computer codes and data files documented.
☒	☐	☐	Data used in calculations explicitly stated in document.
☒	☐	☐	Data checked for consistency with original source information as applicable.
☒	☐	☐	Mathematical derivations checked including dimensional consistency of results
☒	☐	☐	Models appropriate and used within range of validity, or use outside range of established validity justified.
☒	☐	☐	Hand calculations checked for errors. Spreadsheet results should be treated exactly the same as hand calculations.
☐	☐	☒	Software input correct and consistent with document reviewed.
☐	☐	☒	Software output consistent with input and with results reported in document reviewed.
☒	☐	☐	Limits/criteria/guidelines applied to analysis results are appropriate and referenced. Limits/criteria/guidelines checked against references.
☒	☐	☐	Safety margins consistent with good engineering practices.
☒	☐	☐	Conclusions consistent with analytical results and applicable limits.
☒	☐	☐	Results and conclusions address all points required in the problem statement.
☒	☐	☐	Format consistent with applicable guides or other standards.
☐	☐	☒	** Review calculations, comments, and/or notes are attached.
☒	☐	☐	Document approved (for example, the reviewer affirms the technical accuracy of the document).

D.A. Himes

Technical Peer Reviewer (printed name and signature)

Date

- All "no" responses must be explained below or on an additional sheet.
- ** Any calculations, comments, or notes generated as part of this review should be signed, dated and attached to this checklist. The material should be labeled and recorded in such a manner as to be understandable to a technically qualified third party.

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Appendix – Use of Le Chatelier's Rule to Determine the LFL

The mixture LFL is found from the following:

$$\text{Mixture LFL, \%} = \frac{1}{\frac{C_1}{\text{LFL}_1} + \frac{C_2}{\text{LFL}_2} + \frac{C_N}{\text{LFL}_N}}$$

where C_1 , C_2 and C_N are the volume fractions of the flammable constituents in the mixture not including the air and LFL_i are the lower flammable limits for chemical "i" in terms of volume percent. This equation is used in the body of this report.

This equation is derived from Le Chatelier's law (Section 5.1 of *Gas Explosion Handbook*). The *Gas Explosion Handbook* also states that the formula does not work properly for hydrogen and unsaturated hydrocarbons (e.g., alkenes like ethylene, polyolefin's like butadiene and acetylene) and has more error at the upper flammability limit (UFL) than at the LFL.

However, there are specific flammability data on specific mixtures of hydrogen and other gases and vapors that show that Le Chatelier's rule can be applied and the calculated LFLs be reasonably close to the experimental derived LFLs.

Table 2 of the journal article *The Flammability Limits of H_2 -CO- CH_4 Mixture in Air at Elevated Temperatures* provides a comparison of experimentally derived LFL for hydrogen, carbon monoxide and methane mixtures against that calculated using Le Chatelier's rule. The results at 25 °C are

Fuel Composition, Vol%			Lower Flammability Limit	
<u>H_2</u>	<u>CO</u>	<u>CH_4</u>	<u>Experiment</u>	<u>Calculated</u>
20	40	40	6.0	6.16
50	25	25	5.0	5.06
80	10	10	4.2	4.29

The report *Flammability of Gas Mixtures Containing Volatile Organic Compounds and Hydrogen* provides the results of experiments in which the LFL of volatile organic compound-hydrogen mixtures are determined. Mixtures of hydrogen, 1,2-dichloroethane, methyl ethyl ketone, and toluene were tested. Ten combinations of these gases/vapors were tested. Hydrogen fraction of the flammable mixture ranged from 100% to 20%. Another eighteen combinations were tested that did not contain hydrogen. The LFL for each mixture was calculated using Le Chatelier's rule and determined based on experiments. The results of the test with hydrogen are shown on Tables 3 and 4 of the reference and are reproduced below.

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Table A-1. Results of the Determination of the LFL by Experiment and Use of Le Chatelier's rule

Mixture number	Proportion of Compound in Mixture on Air-Free Basis, %				LFL, experiment	LFL, calculated
	DCE	MEK	Tol	H ₂		
5	25	25	25	25	2.4	2.28
6	33	33	0	33	3.4	3.3
12	33	0	33	33	2.65	2.44
14	50	0	0	50	5.35	4.92
20	0	50	0	50	3.15	2.81
24	0	0	50	50	2.05	1.94
26	0	0	0	100	5.0	5.00
29	0	33	33	33	2.0	1.96
39	0	0	50	50	2.05	1.94
40	25	25	25	25	2.4	2.28

DCE = 1,2-dichloroethane
MEK = methyl ethyl ketone
Tol = toluene
H₂ = hydrogen
Note 1: data shown in Table 4 of the reference and was found using Le Chatelier's rule

$$\text{Mixture LFL} = \left[\sum \left(\frac{C_i}{\text{LFL}_i} \right) \right]^{-1} * 100$$

Where C_i = concentration of component "i" in the gas mixture on an air-free basis.

Experiments with hydrogen, methane and carbon monoxide show that the LFL calculated using Le Chatelier's rule is slightly greater (by 1 to 3%) than that found in the experiment.

Experiments with volatile organic compounds and hydrogen show that the calculated LFL is slightly less (5 to 10%) than the actual LFL.

Since mixtures of hydrogen, methane and VOCs are of interest and since the differences between the calculated LFL and the experimental LFL is around plus 3% to minus 10%, use of Le Chatelier's rule for flammability gives reasonable results for the LFL. Le Chatelier's rule can be used for analyzing the flammability of hydrogen and methane and hydrogen and VOC mixtures in waste containers.

References:

Flammability of Gas Mixtures Containing Volatile Organic Compounds and Hydrogen, Journal of Loss Prevention in the Process Industries, Vol 13 (2000), pg 377-384, Elsevier Press, New York, New York.

Gas Explosion Handbook, Journal of Hazardous Materials, Vol 52 (1997), pg 1-150, Elsevier Press, New York, New York.

The Flammability Limits of H₂-CO-CH₄ Mixtures in Air at Elevated Temperatures, International Journal of Hydrogen Energy, Vol 31 (2006), pg 485-489, Elsevier Press, New York, New York.