

Analysis of Relationship Between  
Flammability Limits and TCG (Calculated)

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### Analysis of Relationship Between Flammability Limits and TCG (Calc.)

Background: Using Bunsen absorption coefficients, one can calculate the concentrations of gases above a liquid based on the concentrations present in the liquid. The total combustible gas concentration (TCG) can then be calculated. The flammability limits for those flammable gases found in the dissolved gas analysis (DGA) of mineral oil type insulating fluids are shown below:

<u>Gas</u>	<u>Lower limit</u>	<u>Upper limit</u>
Hydrogen	4.0	75% (v/v)
Methane	5.3	14
Ethane	3.0	12.5
Ethylene	3.1	32.0
Acetylene	2.5	81.0
Carbon Monoxide	12.5	74

(Values taken from the Matheson Gas Handbook)

These values assume that the gas in question is mixed with air and the composition of air is given below:

<u>Gas</u>	<u>Concentration (v/v)</u>
Nitrogen	78.084 %
Oxygen	20.946
Carbon Dioxide	0.033
Argon	0.934
Neon	18.18 ppm
Helium	5.24
Krypton	1.14
Xenon	0.087
Hydrogen	0.5
Methane	2
Nitrous Oxide	0.5

(Values taken from the Handbook of Chemistry and Physics, 58th ed., p. F-210)

Calculations: If one assumes that to form a flammable mixture with air, the oxygen content at the lower limit has to be close to that found in air, i.e. 20%, then one can calculate dilution factors for mixtures that contain less than this value.

Using the ideal gas equation:  $PV = nRT$

where: P is the pressure  
V is the volume  
n is the number of moles  
R is the gas constant  
T is the temperature

(All of the above have to be in appropriate units.)

One can calculate the volume of air,  $V_2$ , that has to be added to a volume,  $V_1$ , of a gas mixture to bring the oxygen content up to a given value. Assuming that the temperature and total pressure remain constant, then the total volume,  $V_3$ , is the sum of the first two volumes, i.e.  $V_3 = V_1 + V_2$ .

From the material balance for oxygen we know that  $n_3 = n_1 + n_2$  and this relationship can be rearranged to relate the volumes and concentrations in the following manner:

$$C_3V_3 = C_1V_1 + C_2V_2$$

where:  $C_3$  and  $V_3$  are the final oxygen conc. and the final total volume of the mixture.  
 $C_1$  and  $V_1$  are the initial oxygen conc. and the initial volume of the mixture.  
 $C_2$  and  $V_2$  are the oxygen conc. in air and the volume of air to be mixed with initial volume of the mixture.

If we now define a dilution factor,  $\beta$ , as the ratio of  $V_2/V_1$ , then it follows that  $\beta = V_2/V_1$ , or in terms of the concentrations then:

$$\beta = (C_3 - C_1)/(C_2 - C_3)$$

Since  $V_2$  is for air, then  $C_2 = 0.21$  and it follows that:

$$\beta = (C_3 - C_1)/(0.21 - C_3)$$

Using this relationship we can calculate a family of linear curves that relate the dilution factor,  $\beta$ , as a function of the initial oxygen concentration,  $C_1$ , for various final concentrations of oxygen,  $C_3$ .

Another factor that will be discussed later is that of the rates of diffusion of various gases. The relative rates of diffusion can be calculated using the kinetic theory of gases that states that at a constant temperature, the relative rates of diffusion are only a function of the gases molecular weight as follows:

$$v_1/v_2 = (M_2/M_1)^{1/2}$$

The following table relates the relative rates of diffusion with reference to that of oxygen:

	M	$M_{O_2}/M$	$v/v_{O_2}$	Diffusion rate rel. to $O_2$
Hydrogen	2	16.00	4.00	+ 300%
Methane	16	2.00	1.41	+ 41%
Ethane	30	1.067	1.03	+ 3%
Ethylene	28	1.148	1.07	+ 7%
Acetylene	26	1.231	1.11	+ 11%
Carbon Monoxide	28	1.148	1.07	+ 7%
Carbon Dioxide	44	0.727	0.85	- 15%
Nitrogen	28	1.148	1.07	+ 7%
Oxygen	32	1.000	1.00	- - -

Discussion: If one looks at the four cases A-D that are identified by our lab ID number and date we can make some general observations. Firstly we can see that the major contributor to the calculated TCG value arises by far from the hydrogen. This is to be expected since hydrogen is the least soluble of these gases in mineral oil while acetylene is the most soluble. Thus hydrogen would have a higher concentration relative to acetylene in the gas blanket (TCG) than in the oil (DGA), e.g.  $5.56/0.40 = 13.9$  ;  $3.05/0.21 = 14.5$  ;  $3.03/0.21 = 14.4$  ;  $2.16/0.15 = 14.4$  for cases A, B, C, and D respectively.

Secondly, a similar situation exists with regard to the oxygen to nitrogen ratio. Since oxygen is about twice as soluble as nitrogen in mineral oil, the ratio of oxygen to nitrogen in the gas blanket (TCG) will be lower than this same ratio in the oil (DGA), e.g.  $0.23/0.39 = 0.59$  ;  $0.20/0.33 = 0.61$  ;  $0.23/0.38 = 0.61$  ;  $0.22/0.36 = 0.61$  for cases A, B, C, and D respectively. This will usually result in the oxygen content calculated in the gas blanket being less than that occurring in air.

Thirdly, if we make the assumption that the lower flammability limit will require an oxygen content,  $C_3$ , of 20% then we can calculate the dilution factor,  $\beta$ , using the calculated oxygen content,  $C_1$ , of the gas blanket further assuming that the oxygen content of air,  $C_2$ , is 21%. Using this approach the dilution factors for cases A, B, C, and D were calculated to be 1.7, 4.1, 1.4, and 3.2 respectively. Another interpretation of the dilution factor,  $\beta$ , is that it is the safety factor one can multiply the normal lower limit of flammability by to determine what the new calculated lower limit of flammability would be for hydrogen in the presence of the oxygen content calculated to actually be in the gas blanket. Using this approach one calculates these new lower limits of flammability for hydrogen to be 6.8, 16.4, 5.6, and 12.8% for cases A, B, C, and D respectively.

Fourthly, all of the above calculations are based on the assumption that the system is at equilibrium within a sealed system. This is obviously not the case in a free breathing type apparatus.

Fifthly, since these systems are free breathing units, it means that while air can diffuse into the system the gases in the blanket can diffuse out of the system. From the diffusion data cited earlier, we can see that all of the combustible gases will diffuse out of the system faster than oxygen will diffuse into the system. This is especially true for the most critical combustible gas, hydrogen. This in effect will work in favor of reducing the chance of having a combustible mixture. It should also be noted that the one gas that will diffuse out of the system slower than the oxygen can diffuse into the system is carbon dioxide, which is non-combustible. This also works in favor of reducing the risk of having a combustible mixture in the gas blanket.

Conclusions: It is obvious that one can not do a direct comparison of the lower limit of flammability given for a mixture with air to the calculated TCG value in the gas blanket. It appears that all of the factors that we have considered above tend to work in the direction that increases the safety factor over that seen by direct comparison. Furthermore the diffusion factors cited above are based only on molecular diffusion and not mass transfer. If one has cross ventilation, then mass transfer should also decrease the concentration of combustible gases even faster. This could be accomplished by having vents on opposite sides of the unit or even providing for forced ventilation.

Appendix:

Case A: Lab ID 103351 (June 3, 1996)

	DGA results	Calc. in Gas Blanket
Hydrogen	529 ppm	1.00 %
Methane	1075	0.35
Ethane	387	0.03
Ethylene	3004	0.30
Acetylene	1330	0.18
Carbon Monoxide	237	0.21
Carbon Dioxide	946	0.15
Nitrogen	66,654	79.50
Oxygen	25,906	18.26
TCG calc.		2.05 %
$\beta$ (for $C_3 = 20\%$ )		1.7
Calc. lower limit of flammability for $H_2$		6.8 %

Case B: Lab ID 1033212 (May 24, 1996)

	DGA results	Calc. in Gas Blanket
Hydrogen	610 ppm	1.19 %
Methane	472	0.15
Ethane	244	0.01
Ethylene	2042	0.20
Acetylene	2860	0.39
Carbon Monoxide	313	0.29
Carbon Dioxide	1600	0.23
Nitrogen	67,363	81.60
Oxygen	22,184	15.92
TCG calc.		2.22 %
$\beta$ (for $C_3 = 20\%$ )		4.1
Calc. lower limit of flammability for $H_2$		16.4 %

Case C: Lab ID 103212 (May 10, 1996)

	DGA results	Calc. in Gas Blanket
Hydrogen	511 ppm	1.00 %
Methane	453	0.15
Ethane	244	0.01
Ethylene	2059	0.21
Acetylene	2401	0.33
Carbon Monoxide	204	0.19
Carbon Dioxide	1321	0.19
Nitrogen	68,646	79.34
Oxygen	25,917	18.57
TCG calc.		1.86 %
$\beta$ (for $C_3 = 20\%$ )		1.4
Calc. lower limit of flammability for $H_2$		5.6 %

Case D: Lab ID 103212 (May 3, 1996)

	DGA results	Calc. in Gas Blanket
Hydrogen	1188 ppm	2.22 %
Methane	2615	0.83
Ethane	635	0.05
Ethylene	6407	0.63
Acetylene	7688	1.03
Carbon Monoxide	216	0.19
Carbon Dioxide	2489	0.34
Nitrogen	67,324	77.93
Oxygen	24,461	16.79
TCG calc.		5.07 %
$\beta$ (for $C_3 = 20\%$ )		3.2
Calc. lower limit of flammability for $H_2$		12.8 %

