Experimental and Empirical Studies Documenting that 25% of LFL Will Not be Exceeded in Laboratories with Laboratory Scale Use of Chemicals

1. Measuring Fume Hood Duct Concentrations of Diethyl Ether

2. USATHAMA Modeling of Ethyl Ether Release Beneath a Chemical Fume Hood

I. Measuring Fume Hood Duct Concentrations of Diethyl Ether

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After submitting to the Office of the State Fire Marshall calculations of concentrations of flammable material fumes in laboratory fume hood ducts that might occur under severe spill conditions, I was asked to confirm these by brief experimental investigations. Since diethyl ether was the chemical with the most dangerous characteristics in the mathematical calculations, it was the material of choice for experimental investigations. The experiment was, briefly, to flood the internal working surface of the fume hood with a layer of diethyl ether and measure concentrations of ether developed in the fume hood duct.

Results: The test results confirmed the calculations. At no point did the duct concentration rise above 10% of the LFL/LEL of diethyl ether. The 30 second time point was almost identical with the 2 minute sample and the sample taken at 4 minutes was lower by 30% due presumably to evaporative cooling. The final point showed the duct concentration dropped to near zero shortly after the ether was removed from the hood.

Data: The standards, A, B, and C, calculated out to be 0.0%, 0.355%, and 0.712% diethyl ether in air respectively. Diethyl ether's LEL/LFL is reported at 1.85% in air so 10% of the LEL would be a concentration of 0.185%.

Sample Name	component	RT(min)	area units	% in air	LEL/10
Standard A (zero)	Air ethyl ether	.41 -NS-	3631 -0-	0.000%	
Standard B (0.5µl)	Air ethyl ether	.41 .68	3054 4557800	0.355%	
Standard C (1.0µL)	Air ethyl ether	.41 .67	2613 9057700	0.712%	
Sample A-1 (0-5 min)	Air ethyl ether	.41 .68	2808 645680x3.2	0.161%	0.185%
Sample B-1 (2.0 min)	Air ethyl ether	.41 .68	2695 662520x3.2	0.165%	0.185%
Sample D-1 (4.0 min)	Air ethyl ether	.41 .68	2914 462340x3.2	0.115%	0/185%
Sample C-1 (15 min)	Air ethyl ether	.41 .69	3074 11812x3.2	0.003%	0.185%

Experimental Details: The experiment took place in a fume hood of the newer air-saving design with a nominal 6-foot width (approximately 10 sq. ft. work area) and an average face velocity of 85-90 LFM (vertical sash down and maximum horizontal sash opening). The laboratory ambient temperature was 23^{o} C (degrees centigrade). Sampling was accomplished by syringe withdrawal approximately 15 linear feet down the hood duct from the connection point to the hood unit. Sampling was 10cc using a 6: needle to reach the approximate center of the hood duct and was done through a small (1/8") opening. The samples were injected into a partially evacuated septum vial of 32cc volume. This resulted in a 3.2 to 1 dilution factor used in the above data calculations. After the samples were added the vials were at or near ambient pressure. Approximately 1 liter of anhydrous diethyl ether was poured on the hood surface at time=0.0 and allowed to begin evaporating. At time=30 seconds the first 10cc sample was taken and at time=2 minutes a second sample was withdrawn. Between the first and the second time points additional ether was added to maintain the flooded condition (approximately 600 additional mL) as the evaporation was apparent. The evaporation chilled the hood work surface quickly and the third sample point was anticipated to have a lower concentration than the first two. After five minutes time the ether was removed and the hood allowed to air for an additional ten minutes and a final sample was taken (time=15 minutes).

The sample vials were taken to a laboratory equipped with a Varien model 3700 Gas Chromatograph and using a flame ionization detector the samples were compared to a zero pt. sample and two standards prepared using 0.5 microliters (0.355%) and 1.0 microliters (o.712%) respectively. All injected samples were 0.1cc in volume. The GC employed an 8' long glass column (3mm ID) packed with 10% SP2250 on 100/120 mesh Supelcoport. The column was maintained at 65^{o}C (isothermal) with an injection port and detector temperature of 200^{o}C. Carrier gas was Helium at 27cc/minute. Data was collected by a HP 3390A integrating recorder. Any questions or comments can be directed to me at UCSD Department of Chemistry, (619) 534-5906

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Note: please see attached “Addendum” which was a supplement to a previous letter to the State Fire Marshall’s office on this issue. The addendum simply shows that the Cameo II air model program gave reasonable theoretical results and the subsequent testing performed and detailed above supports the calculations submitted earlier.

Addendum

As mentioned in the accompanying letter the issue of fume hood duct sprinklering has led to several significant questions. Of some significance was whether it would be possible to approach the LFL or LEL of some of the more volatile laboratory solvents in the fume hood duct system if possible, but highly unlikely accident circumstances should arise.

This is a brief summary of the approach used to examine the question.

Employing some backwards-logic the first question asked was what materials, particularly the ubiquitous ones in research environments, presented the greatest risks in terms of their physical properties. Acetone and diethyl ether were chosen because of their low boiling points, LFL's and high vapor pressures under normal ambient conditions and because they are so commonly encountered (increasing the likelihood that if an accident were to occur, these materials might be involved). Acetone shows an LEL of 2.6%, an FLP of 1.4^{o}F, and a BP of 133^{o}F. Diethyl ether has a lower LFL at 1.9%, FLP at -40^{o}F, and a BP of 95^{o}F.

Stretching realism to the extreme, an accident of very high improbability in terms of quantity and spill area was examined employing the following conditions: 6' energy efficient fume hood, lab temperature elevated to 80^{o}F, spill of material sufficient to cover 10 sq. ft. (approximate size of entire hood base pan), and an air flow volume of 770 cubic ft/min at a face velocity of 100 lfm or 1.2 MPH. Most of the evaporation rates were obtained from the CAMEOII "ALOHA" air model from NOAA's Hazardous Materials Unit.

The volume of air flowing in the duct is 770 cfm prior to any secondary dilution points so the volume of ether need to reach the LPL (1.9%) would be 1.9% of 770 or 14.6 cfm. Using an ideal gas model (PV=nRT) that 14.6 cubic ft or 413 liters of ether would represent about 17 moles of ether or (17 mol x 74g/mol)/28.4g/oz.=44oz. (Over 2.5 pounds per minute). That translates directly to 4.4 oz. per minute of ether evaporating up the fume hood to reach 10% of the LFL.

Using the puddle model of CAMEOII/Aloha Program under energy balance conditions (takes into account the cooling effect of evaporating liquid) the evaporation rate of a 10 sq.ft. puddle at an indoor location would be in the vicinity of 2.6 oz./minute or lower than 10% of the LFL (using the complete cloud cover option since solar radiation would not be present).

When acetone is examined, the evaporation rate is approximately 1.4 oz./min., for the above conditions which is much lower than the 4.7 oz./min. resulting from calculations of 10% of the LFL.

Obviously, to reach the LPL for either of these materials is an almost impossible situation under any foreseeable accident scenarios.

With questions of useful functionality, maintenance problems, and flow impediments associated with duct sprinkler heads and the likelihood they would serve as long term material condensation sites it would seem prudent to exercise caution in considering their installation. In a flash fire situation (in the ductwork) there would be some doubt as to reliable activation of sprinkler heads and even if they did activate their operation and subsequent water flow could result in even worse fire situations and spreads of hazardous materials from the fume hood or hoods served by the ductwork.

II. USATHAMA Modeling of Ethyl Ether Release Beneath a Chemical Fume Hood

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A vapor emission model released by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) for estimating vapor emissions from an accidental spill is used in conjunction with the principle of mass conservation to estimate the ethyl ether concentrations in the chemical fume hood exhaust ductwork. The approach takes into consideration the physics of chemical evaporation, major parameters affecting the evaporation process and empirical test results of many chemical spills in the laboratories. This is a conservative model that will tend to overestimate airborne concentrations relative to numerous other available emission models.

The model and calculations are presented below. The ethyl ether concentration in the exhaust ductwork is estimated to be 4,448 ppm at a ventilation rate of 850 cfm. This concentration is below 4,750 ppm, [25% of ethyl ether's lower explosive limit (LEL)]. A potential fire hazard in the exhaust ductwork can be completely avoided without a fire suppression system if the ventilation rate of the exhaust ductwork system is maintained at a flowrate of 850 cfm or above.

The Gauss model (Rife, 1981), which was developed for USATHAMA using equations for three-dimensional diffusion and two-dimensional vaporization into flowing air, is employed for estimating the vapor emission rate of ethyl ether from a spill in a chemical fume hood. For chemical evaporation from a square area, the model takes the following form:

$$E_{spill} = 169\ (1 + 0.51\ Re^{1/2}\ Sc^{1/3})\ *Pv/P * (MW)/T_a * D_{air} * l$$

Where:

E_{spill} = vapor emission rate of ethyl ether, in g/min;
Re = Reynolds number, Re = u Gl/I * 10^4
Sc = Schmidt number, Sc = I/GD $_{air}$;
U = wind speed on the surface of the spill, m/sec;
I = air viscosity, 0.00018 g/cm-sec (Rife 1981);
G = air density, 0.00119 g/cm^3 (Rife 1981)
l = length of the square, in meters;
T_a = ambient temperature, 298 degrees K (25 degrees C);
D_{air} = air diffusivity for ethyl ether, 0.093 cm2/sec (USEPA 1987);
MW = molecular weight of ethyl ether, 74.1 g/gmole (USPEPA 1987);
P_v = vapor pressure of ethyl ether, 440 mm Hg (NIOSH 1994); and
P = atmospheric pressure, 760 mm Hg.

For a rectangular shape area, the vapor emission rate of ethyl ether can be calculated by multiplying Equation 1 by the ratio of the long side to the short side of the rectangle (Rife 1981). Therefore, the ethyl ether emissions from a spill on a 5'6" by 2'2" (168 cm by 66 cm) surface in a fume hood would be:

$E_{spill} = (168/66) * (1 + 0.51\ Re^{1/2}\ Sc^{1/3}) * Pv/P * (MW)/T_a * D_{air} * l$

The air current above a spill in the chemical fume hood is a function of the exhaust ventilation rate. The air current could be approximated by dividing the exhaust flow rate by the hood opening. A typical hood opening for the 6-feet CFHs indicated for the Commercialization Center is estimated to be 5'6" wide and 1'6" high with an opening area of approximately 8.25 ft^2. Therefore, the air current corresponding to an exhaust ventilation rate of 825 cfm would be 100 ft/min (0.508 m/sec). The ethyl ether vapor emissions resulting from a spill in a chemical fume hood could be calculated as follows:

$E_{spill} = (168/66) * 169\ [1 + (0.51) * (22166)^{1/2} (1.626)^{1/3}] * (440/760) * (74.1/298) * (0.093) * 0.66$

$E_{spill} = 2.545 * 169\ [1 + (0.51) * (148.9) * (1.176)] * (0.579) * (0.2486) * (0.093) * (0.66)$

$= 430.1 * [90.3] * 0.008835$

$E_{spill} = 343$ g/min.

where the Reynolds number and Schmidt number computed below are used in the above calculation:

$Re = (0.508) * (0.66) * (0.00119) * 10^4 / 0.00018$

$= 22166$, and

$Sc = (0.00018)/(0.00119)/(0.093)$

$Sc = 1.626$

Concentration Estimation

$C_{exhaust} = E_{spill}/Q_{air\ flow}$

where

$C_{exhaust}$ = ethyl ether concentration in the ductwork, g/m^3.

E_{spill} = ethyl ether emission rate, in g/min; and

$Q_{air\ flow}$ = air current in the ductwork, 23.36 m^3/min (or 850 cfm).

The ethyl ether concentration in the ductwork is calculated to be

$C_{exhaust}$ =343 g/min / 23.36 m^3/min

$C_{exhaust}$ = 14.68 g/ m^3

$C_{exhaust}$ = 4448 ppm of ethyl ether or 0.4448%. The LEL for ethyl ether is 1.9% and 25% of the LEL is 0.475%. $C_{exhaust}$ is less than 0.475%.

Where 1 ppm of ethyl ether at room temperature = 3.03 mg/ m^3 of ethyl ether is used in converting the mass concentration to volume concentration.

References:

1. Rife, R.R. 1981. *Calculation of evaporation rates for chemical agent spills*. Environmental & Safety Division. US Army Toxic and Hazardous Materials Agency. Report DRXTH-ES-TM-8110.

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3. United States Environmental Protection Agency (U.S. EPA). 1987. Office of Air Quality Planning and Standards. *Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)- Air Emission Models.* U.S. EPA-450/3-87-026. Research Triangle Park, North Carolina. December.