Ontario Air and Noise Best Practices

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Solvent Storage tanks may emit a contaminant to the environment and therefore require approval under Section 9 of the Environmental Protection Act. Applicants must show that the equipment to be approved is capable of operating in compliance with the Act, Regulations and guidance material. Practitioners will as a best practice use the following examples of how to estimate the emission from solvent storage tanks in supporting information for applications for a Section 9 CofA in order to facilitate the Section 9 reviewer's review of the application. Practitioner will use the template excel spread sheet to document the calculations.

Practice

There are generally three times when waste tank vapours are emitted to the surrounding environment. Those three times are when something is added to the tank, when the tank is emptied, and when the tank warms (breathing losses). In the second case, the emissions leave the vent on the truck or process area rather than the vent on the waste storage tank.

> NB: This best practice only applies to solvents that have a vapour pressure of greater than 1 kPa; in accordance with Ontario Ministry of Environment ("MOE") accepted practice (Procedure for Preparing an Emission Summary and Dispersion Modelling Report, June 2005) low temperature handling of non volatile liquids can be considered negligible under s.8 of O. Reg. 419/05.

There are two parameters for these emissions: the volume emitted and the concentration of each contaminant in the emitted volume. These two parameters are discussed below, followed by an example of the calculations performed for the emission concentrations.

Volume Emitted

The volume of vapour emitted when filling a waste tank will be the same as the volumetric flow rate of the liquid entering the tank as long as the liquid entering the tank is not under pressure. If the liquid is under substantial pressure then there is the potential for a component to flash upon entering the tank. This discussion assumes that the liquid is not pressurized.

The volume of vapour emitted from a waste truck is the same as the volume of liquid entering the truck. This volume should correspond to the volume leaving the waste tank.

The emission from the tank caused by warming will depend on the volume of vapour in the tank and the change in temperature experienced by the liquid and vapour in the tank. If you assume that the Ideal Gas Law applies, the vapour in the tank will expand proportionally to the change in temperature (in degrees Kelvin) as it is heated.

All three options should be evaluated to determine which provides the maximum emission rate. In

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most cases, the scenario that will result in the maximum emission rate will occur when filling or emptying the tank because the flow rate tends to be higher. These two scenarios are also the easiest to evaluate because they are the flow rate of the respective pumps. A typical truck pump has a volumetric flow rate of 50 US Gallons per minute.

Concentration of Each Contaminant

A normally reasonable assumption is that the concentration of a contaminant in the vapour phase is proportional to the mole fraction of that contaminant in the liquid times its vapour pressure. If both the liquid and vapour phase are ideal, then this relation is known as Raoult's Law[1].

In a waste tank, Raoult's law will normally provide a good estimate of the vapour phase concentration because the vapour phase has reached equilibrium and the liquid entering the tank is likely of similar composition to the liquid already in the tank.

In a waste transfer truck, the assumption that the emission has a Raoult's Law relationship to the liquid entering is less likely because the vapour in the truck is more likely to be related to the last load rather than the current one. Alternatively, if the truck was clean prior to loading from your waste tank, the initial emission would be of clean air. Assuming that the emission has a Raoult's Law relationship to the liquid is conservative because it over predicts the clean truck scenario. The emission from a previous load is generally unpredictable but most collection companies tend to pick-up the same kind of solvents in the same truck. Therefore, the most conservative assumption for the facility is to assume that the emission has a Raoult's Law relationship with the vapour emission of the waste tank at your facility because that increases the contaminants already emitted at your facility.

A waste tank will generally warm over the day. As the temperature of the liquid increases, the vapour pressure of the liquids will increase but the vapour pressure of some contaminants may increase faster than others. As a result, the composition will change as the temperature increases. However, the change in liquid temperature is generally less than 5 degrees over the day so this change in temperature may not change the vapour composition appreciably.

Sample Vapour Phase Emission Calculation

Assume the facility empties the waste tank at 50 US Gallons/min to the truck. The solvent transfer takes more than 30 minutes so there is no reduction available from averaging the total emission over 30 minutes. Since the vapour emission rate is the same as the liquid transfer rate, the emission from the waste tank vent is 50 US Gallons per minute (3.15 L/s) of saturated vapour at 20 °C (293.15 K) and atmospheric conditions. This temperature is generally higher than expected in an external tank in Ontario even in the summer but the saturated vapour pressure is generally published at 20 °C or 25 °C

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[1] David M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, Fourth Edition, Prentise-Hall of Canada Ltd, Toronto, 1982.

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so the emission calculated will be conservatively high.

Assume the liquid in the waste tank has the following composition:

Contaminant	Saturated Vapour Pressure (mmHg)[2]	Molecular Weight (g/g-mole)	Weight % Composition (Mass basis)
Toluene	22.4	92.13	65%
Xylene	6.4	106.16	30%
Methanol	94.7	32.04	5%

If we use a basis of 1 kg of solvent, the moles of each contaminant is calculated as

Moles Contam /kg Solvent = "Weight % Composition" / "Molecular Weight". The "Total Moles" in 1 kg of solvent is the sum of all these values. So,

$$\text{Moles of Toluene/kg of Solvent} = \frac{\text{Weight \% Composition}}{\text{Molecular Weight}} = \frac{0.65 kgToluene}{\dfrac{92.13 kgToluene}{kg-mole}}$$

Moles of Toluene/kg of Solvent = 0.007055 kg-moles

Similarly,
Moles of Xylene/kg of Solvent = 0.002826 kg-moles
Moles of Methanol/kg of Solvent = 0.001561 kg-moles
The total moles = 0.007055 + 0.002826 + 0.001561 = 0.01144 kg-mole

The liquid phase mole fraction (F) = moles of contaminant in liquid phase/ total moles in liquid phase so the liquid phase mole fraction for toluene is 0.007055 / 0.01144 = 0.62.

Similarly,
xylene is 0.002826 / 0.01144 = 0.25
methanol is 0.001561 / 0.01144 = 0.14

For an ideal gas, the Ideal Gas Law[3] says PV=nRT

Where:
    P = Pressure of the gas (101.3 kPa at atmospheric pressure)

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[2] Robert H. Perry, Perry's Chemical Engineer's Handbook, 7th Edition, McGraw-Hill, 1997.
[3] David M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, Fourth Edition, Prentise-Hall of Canada Ltd, Toronto, 1982.

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V = Volume of gas (in L)
n = moles of gas (in g-mol)
R = 8.314 kPa L/g-mol K
T = Temperature (in Kelvin)

And, $n = M/M_{wt}$

Where:
n = moles of gas (in g-mol)
M = mass of gas (in g)
M_{wt} = molecular weight of the contaminant (in g/g-mol)

So the mass emission rate of the contaminant from the tank is $M = M_{wt}PV/RT$.

Since the partial pressure of the contaminant is the liquid mole fraction times the pure vapour pressure ($P=P_v*F$), then $M = M_{wt}*P_v*F*V/RT$.

For toluene:

$$M_{toluene} = \left(\frac{\frac{92.13\,\text{g}}{\text{g-mol}} * 22.4\text{mmHg} * \frac{0.62\text{g-mol toluene}}{\text{g-mol mixture}} * \frac{3.15L}{s}}{\frac{8.314\text{kPa L}}{\text{g-mol K}} * 293.15K} \right) * \left(\frac{101.3kPa}{760mmHg} \right) = 0.2195 g/s$$

Similarly, $M_{xylene} = 0.02895$ g/s and $M_{methanol} = 0.07139$ g/s.

In a spreadsheet shown at the end of this section, the above information is repeated in table form.

The columns in the Table show the following information.
- CAS# – CAS# for the contaminant
- Contaminant name – Name of the contaminant in this column.
- Saturated Vapour Pressure – pure component saturated vapour pressure.
- Molecular Weight – molecular weight of the contaminant.
- Weight % – percent of total mass for this contaminant. Usually based on analysis.
- Moles Contam /kg Solvent – calculated as the "Weight %" / "Molecular Weight". The "Total Moles" in 1 kg of solvent is the sum of all these values and is shown at the bottom of the column.
- Vapour Mole Fraction – the "Moles Contam /kg Solvent" / "Total Moles".
- ½ Hour Average Emission Rate – calculated as ("Saturated Vapour Pressure" * "Vapour Mole Fraction" * "Bulk Filling Rate" * "Molecular Weight" / (R * Tank Temperature) * "Units Conversion for Pressure" where R=8.314 kPa L/g-mol K, T=293.15 K, and "Units Conversion for

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Pressure"=101.3 kPa/760 mmHg.
- Bulk Filling Rate – the rate at which the tank is filled in both US and SI units (shown at the bottom of the table).
- Tank Temperature – the temperature of the tank in K (shown at the bottom of the table).

Table

CAS#	Contaminant	Saturated Vapour Pressure (mm Hg)	Molecular Weight (g-mol)	Weight % (%)	Moles Contam /kg Solvent (g-mol)	Vapour Mole Fraction	½ Hour Average Emission Rate (g/s)
108-88-3	Toluene	22.4	92.13	65%	0.007055	0.62	0.21951
1330-20-7	Xylene	6.4	106.16	30%	0.002826	0.25	0.02895
67-56-1	Methanol	94.7	32.04	5%	0.001561	0.14	0.07139

Total Moles: 0.0114

Bulk Filling Rate:	50	USGal/min
Bulk Filling Rate:	3.15	L/s
Tank Temperature:	293.15	K

References

1 Procedure for Preparing an Emission Summary and Dispersion Modelling Report, June 2005
2 Robert H. Perry, Perry's Chemical Engineer's Handbook, 7th Edition, McGraw-Hill, 1997.
3 David M. Himmelblau, Basic Principles and Calculations in Chemical Engineering, Fourth Edition, Prentise Hall of Canada Ltd, Toronto, 1982

Conclusions

The above sample calculations are expected to allow practitioners to estimate from Raoult's Law and literature vapour pressures the concentration of vaporous emissions from a tank containing a mixture of contaminants. This standard methodology will speed the review by the MOE.

Notes

The accuracy of the above calculations is dependant on both the accuracy of the vapour pressures used and the accuracy of the assumption that the mixture follows Raoult's Law.

If further assistance is required please contact the Best Practices Committee.

Best Practice developed by Harvey Watson, DJA Environmental Consultants Inc.