CHANGE IN VAPOR CONCENTRATIONS EMITTED FROM MULTICOMPONENT ORGANIC SOLVENTS

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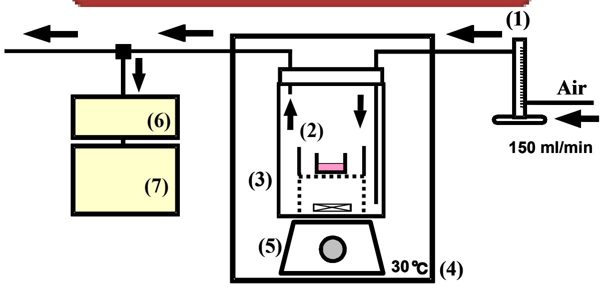
Introduction

- Most organic solvents used in the work environments are mixtures of several solvents. When **mixed solvents** in a open vessel **evaporates continuously**, the vapor concentrations of more volatile components are high at first, then decrease with time. On the contrary, the concentrations of less volatile components are low at first and then it increase. Thus, because generation rate of vapors is changing with time, **to understand behavior of generated vapors are very important** to control work environment in good condition.
- We have been studied to develop **a model for predicting vapor concentrations** emitted from multi-component organic solvents based on theories of **vapor-liquid equilibria** and **mass transfer rate**.

Objectives

- To **investigate generation characteristics** of multicomponent vapors from open vessel that contains mixed solvents.
- To **develop a prediction method** of change in vapor concentrations evaporating from mixed solvents including initial transient period.

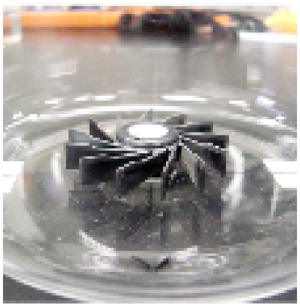
Schematic diagram of experimental apparatus



(1) Flow meter, (2) Evaporator, (3) Vapor generator, (4) Thermostatic bath, (5) Stirrer, (6) Auto gas sampler, (7) FID-gas chromatograph

Photo of the vapor generator

(a) Vapor generator

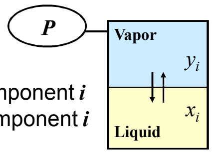


(b) Stirrer for mixing of generated vapors

Vapor-liquid equilibria

When two or more components of liquid solvents are put into a closed vessel, relationship between vapor phase and liquid is expressed as Eq.(1) when equilibrium state is established.

$$P_i^* = y_i P = \gamma_i x_i P_i^{sat} \qquad (1)$$



x_i : liquid phase molar fraction of component i
y_i : vapor phase molar fraction of component i
γ_i : activity coefficient
P_i^{sat} : saturated vapor pressure of component i (Pa)

Activity coefficient (γ_i) in Eq.(2) was calculated from following **UNIFAC equation**:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad (2)$$

Combinatorial component of UNIFAC equation

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \left(\frac{z}{2}\right) q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (3)$$

$$l_i = \left(\frac{z}{2}\right)(r_i - q_i) - (r_i - 1) \quad (4)$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \ (5), \quad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \ (6), \quad r_i = \sum_k \nu_k^{(i)} R_k \ (7), \quad q_i = \sum_k \nu_k^{(i)} Q_k \ (8)$$

Q_k: group surface area, R_k: volume contributions, $\nu_k^{(i)}$: number of occurrences of the functional group on each molecule, z : coordination number (=10)

Residual component of UNIFAC equation

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (9)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \quad (10)$$

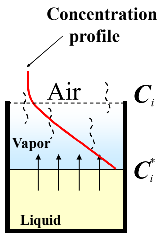
$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \ (11), \quad \Psi_{mn} = \exp\left(-\frac{a_{mn}}{T}\right) \ (12), \quad X_m = \frac{\sum_i x_i \nu_m^{(i)}}{\sum_i x_i \sum_n \nu_n^{(i)}} \ (13)$$

a_{mn} : net energy of interaction between groups m and n, T :absolute temperature

Vapor Generation Rate

At a steady state, mass balance equation is shown as Eq.(14):

$$n \frac{dx_i}{dt} = k_i A (C_i - C_i^*) \times 10^{-6} \quad (14)$$



n: Total mole of liquid

x_i: Liquid molar fraction of component i

k_i: Mass transfer coefficient of component i (mol/min·mm²)

A : Area of vapor-liquid interface (mm²)

C_i^*: Equilibrated vapor concentration (ppm)

P_i^*: Equilibrated vapor pressure (Pa)

$$C_i^* = 0.1013 P_i^* \quad (15)$$

Determination of mass transfer coefficient

For single component, mass transfer coefficient, k, is written as;

$$k = \frac{1}{A(C - C_{sat})} \frac{dn}{dt} \times 10^6 \quad (16)$$

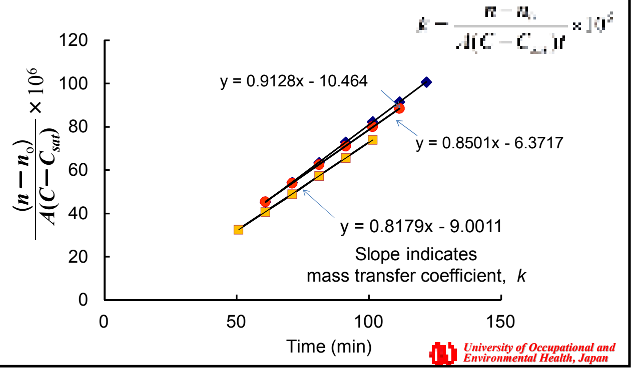
After steady state is established, dn/dt was a constant. Therefore;

$$k = \frac{n - n_0}{A(C - C_{sat})t} \times 10^6 \quad (17)$$

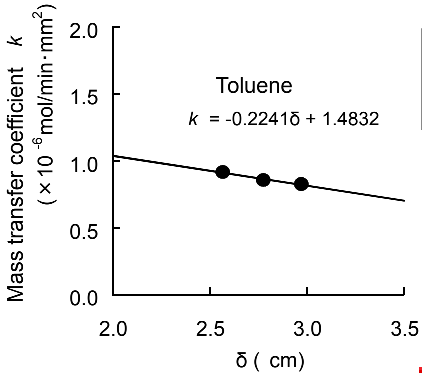
where, C_{sat} is the saturated vapor concentration, n_0 is the amount of initial solvent.

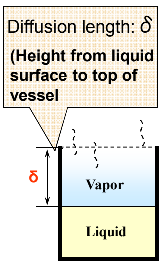
When we plot $(n - n_0)/(A(C - C_{sat})t)$ vs t, the slope of regression line indicates mass transfer coefficient

Determination of mass transfer coefficient



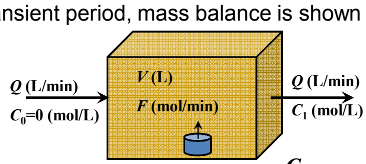
Effect of diffusion length on mass transfer coefficient





Estimation of vapor concentration at initial transient period

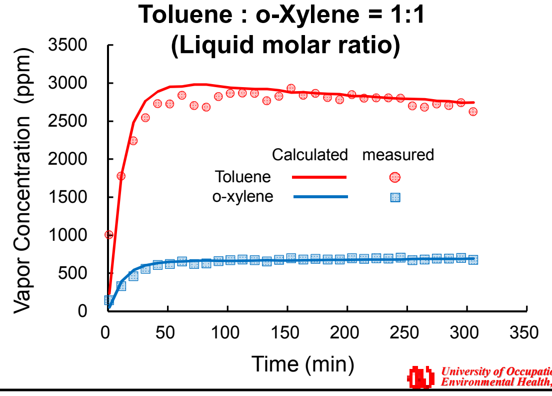
At the beginning of generation, vapor generation is not a steady state and generation rate is largely changing with time. In this transient period, mass balance is shown as:



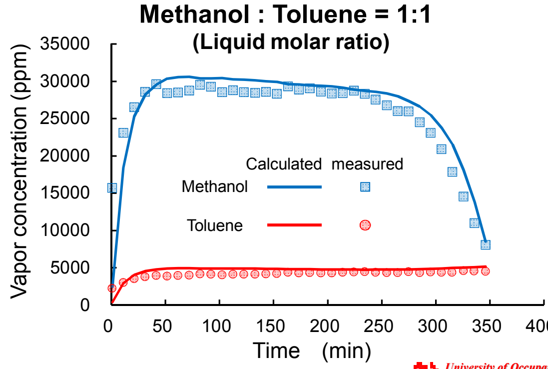
$$V \frac{dC}{dt} = F + C_0 Q - C_1 Q \quad (18) \qquad f = \frac{C_1}{F/Q} = 1 - e^{-\frac{Q}{V}t} \quad (19)$$

$$C_i^{cal}\,(\text{ppm}) = f \times n \frac{dx_i}{dt} \times \frac{22.4}{Q} \left(\frac{T}{273} \right) \times 10^6 \quad (20)$$

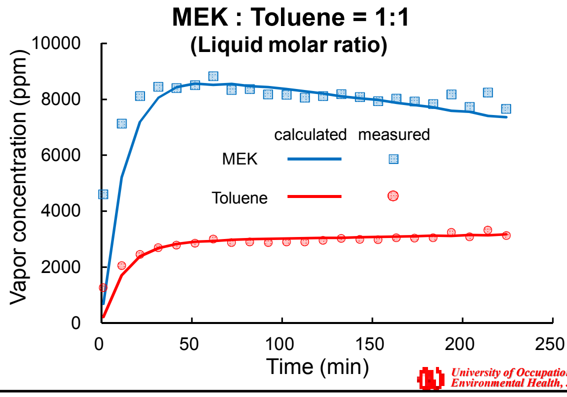
Change in vapor concentration for two-component system



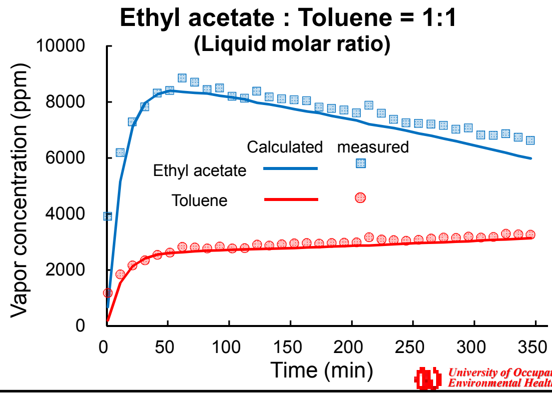
Change in vapor concentration for two-component system



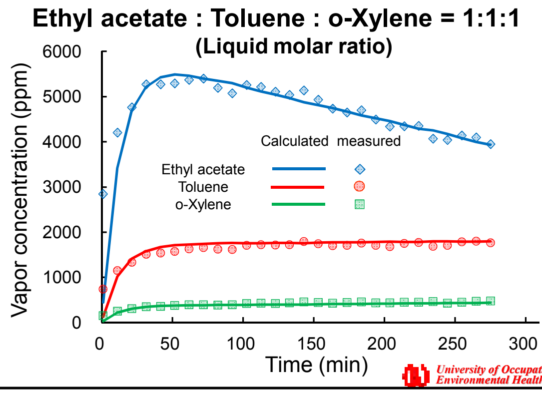
Change in vapor concentration for two-component system



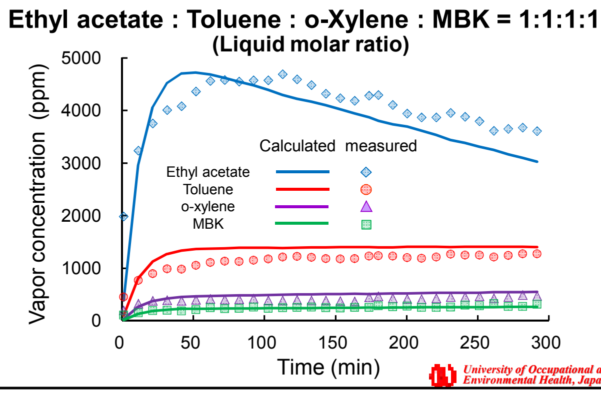
Change in vapor concentration for two-component system



Change in vapor concentration for three-component system



Change in vapor concentration for four- component system



Conclusion

- Vapor concentrations emitted from a vessel contains **two- to four-component of organic solvents** were measured temporally.
- A model for predicting organic vapors are developed based on theories of **mass transfer** and **vapor-liquid equilibria**.
- The calculated vapor concentrations were in good agreement with the experimental ones, indicating that this model can become a **useful tool for risk assessment** of works using organic solvents.