



Estimation of the rate of VOC emissions from solvent-based indoor coating materials based on product formulation

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Abstract

Two computational methods are proposed for estimation of the emission rate of volatile organic compounds (VOCs) from solvent-based indoor coating materials based on the knowledge of product formulation. The first method utilizes two previously developed mass transfer models with two key parameters – the total vapor pressure and the average molecular weight for total volatile organic compounds (TVOCs) – being estimated based on the VOC contents in the product. The second method is based on a simple, first-order decay model with its parameters being estimated from the properties of both the source and the environment. All the model parameters can be readily obtained. Detailed procedures for computing the key parameters are described by using examples. The predictive errors were evaluated with small chamber data, and the results were satisfactory. Thus, the proposed methods provide a way to predict the VOC emissions in the indoor environment without having to conduct costly chamber testing. The two proposed methods work for both TVOCs and individual VOCs. Pros and cons for each method are discussed. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Solvent-based interior coating materials have long been recognized as a major source of volatile organic compounds (VOCs) in the indoor environment (Sterling, 1984). They usually contain more than 25% of the solvent that will be released into the air during the drying period. The most commonly used solvent in these products is mineral spirits – a type of petroleum distillate consisting of aliphatic hydrocarbons with a trace amount of aromatics (Howe-Grant, 1996). Other VOCs are some-

times added to the formulation to enhance its performance, including oxygenated hydrocarbons (such as alcohols), nitrogenated hydrocarbons (such as methyl ethyl ketoxime), and other solvents (such as toluene). Some of the solvent components are identified as hazardous air pollutants (HAPs) in the Clean Air Act Amendments of 1990 (U. S. Public Law 101-549, 1990). The increased exposure to those HAPs and the subsequent health risk are of special concern when solvent-based coatings are used in the indoor environment.

Small environmental chambers have been used to determine the VOC emissions from interior coatings (ASTM, 1995a). The cost of chamber testing could be very high because characterization of emission patterns

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requires multiple samples over time and this is especially true when the emissions of individual VOCs are to be quantified. A tremendous amount of time and resources can be saved if the emission rates can be predicted based on the properties of the source and those of the environment.

This paper presents two methods that can be used to predict the emissions of TVOCs and individual VOCs from solvent-based indoor coatings. They are both based on gas-phase mass transfer theories but differ in complexity.

The proposed methods should be useful in exposure estimation and risk assessment for they can predict indoor VOC emissions with reasonable accuracy without having to rely on costly chamber testing. These methods should also be useful to manufacturers in developing low-emission products for, once the concentrations of predominant VOCs in a product are known, all the information needed to predict the VOC emission rates is known.

2. Literature review

Among all available source models for emissions from indoor coating materials, the first-order decay model is the simplest and most widely used (ASTM, 1995a):

$$E = -\frac{dM}{dt} = E_0 e^{-kt}, \quad (1)$$

where E = emission factor, $\text{mg m}^{-2} \text{h}^{-1}$,

M = amount of VOCs remaining in the source, mg m^{-2} ,

E_0 = initial emission factor, $\text{mg m}^{-2} \text{h}^{-1}$,

k = first-order decay rate constant, h^{-1} , and

t = time, h.

This model has several variations, one of which (Clausen, 1993) is

$$E = -\frac{dM}{dt} = M_0 k e^{-kt}, \quad (2)$$

where $M_0 = E_0/k$ is the amount of VOCs applied, mg m^{-2} .

The major advantage of this family of models is their simplicity. If the air exchange flow rates remain constant, there are analytical solutions to indoor concentrations (Tichenor and Guo, 1991; Evans, 1996). For a single air zone, the solution is

$$C = \frac{SE_0}{V(N-k)}(e^{-kt} - e^{-Nt}) \quad (\text{if } N \neq k), \quad (3)$$

$$C = \frac{SE_0 t}{V} e^{-Nt} \quad (\text{if } N = k), \quad (4)$$

where C = indoor concentration, mg m^{-3} ,

S = source area, m^2 ,

V = room volume, m^3 , and

N = air exchange rate, h^{-1} .

The first-order decay model has two major drawbacks, however. First, estimation of parameters E_0 and k often relies on costly chamber tests. Second, as an empirical model, it is difficult to scale-up.

Efforts have been made to overcome these problems. Clausen (1993) found that, for a given product, the decay rate constant k is inversely proportional to the wet film thickness:

$$k = \frac{k_{E1}}{\theta}, \quad (5)$$

where θ = wet film thickness, μm , and

k_{E1} = decay rate constant for an evaporative source with wet film thickness of 1 μm , $\mu\text{m h}^{-1}$.

This equation provides a way to adjust k when the wet film thickness changes.

Chang and Guo (1994) reported that, for individual VOCs in a given product, the decay rate constant k can be related to their vapor pressure P :

$$\frac{k_1}{k_2} = \frac{P_1}{P_2}. \quad (6)$$

Such a correlation allows estimation of k for one compound relative to another.

Another development allows estimation of k based on the drying time of the solvent (Evans, 1996). Integrating Eq. (2) yields:

$$M = M_0 e^{-kt}. \quad (7)$$

If the drying time, t_D , is defined as the time needed for 90% of the solvent to evaporate, then Eq. (7) becomes

$$0.1 M_0 = M_0 e^{-kt_D} \quad (8)$$

or

$$k = -\frac{\ln(0.1)}{t_D}. \quad (9)$$

Two mass transfer models were introduced to solve the scale-up problem. One, known as the VB model, is for TVOC (Tichenor et al., 1993) and the other, known as the VBX model, for individual VOCs (Guo et al., 1998). These two models are discussed further in the following section.

The gas-phase mass transfer coefficient, which appears in both the VB and VBX models, plays an important role in controlling the rate of VOC emissions from wet sources (Guo et al., 1996). Two theoretical models have been developed to estimate this parameter in indoor environments (Sparks et al., 1996; Zhang et al., 1996). Sparks et al. proposed a simple formula based on the correlation

of Nusselt and Reynolds. Zhang et al. reported a slightly more complex formula, which takes into consideration such additional factors as the boundary layer flow condition and the wall shear stress.

To date, no reported methods allow estimation of emission rates for either TVOCs or individual VOCs based on information about the product formulation. The two methods proposed in this paper attempt to fill this gap.

3. Description of the methods

3.1. Method 1

Method 1 utilizes the VB model (Tichenor et al., 1993) for TVOCs (Eq. (10)) and a modified VBX model for individual VOCs (Eq. (11)):

$$E = k_m(C_{v0} \frac{M_T}{M_{T0}} - C), \quad (10)$$

where k_m = gas-phase mass transfer coefficient for TVOCs, m h^{-1} ,

C_{v0} = initial airborne TVOC concentration at air/source interface, mg m^{-3} , based on the total vapor pressure of the TVOCs,

M_T = amount of TVOCs remaining in the source, mg m^{-2} ,

M_{T0} = amount of TVOCs applied, mg m^{-2} , and

C = TVOC concentration in the bulk air, mg m^{-3} .

$$E_i = k_{mi}(C_{vi} \frac{M_i}{M_T} \frac{\bar{m}}{m_i} - C_i), \quad (11)$$

where E_i = emission factor for component i , $\text{mg m}^{-2} \text{h}^{-1}$,

k_{mi} = gas-phase mass transfer coefficient for component i , m h^{-1} ,

C_{vi} = airborne concentration of component i at air/source interface, mg m^{-3} , based on the vapor pressure of component i ,

M_i = amount of component i remaining in the source, mg m^{-2} ,

\bar{m} = average molecular weight for the organic solvent, g mole^{-1} ,

m_i = molecular weight for component i , g mole^{-1} , and

C_i = concentration of component i in the bulk air, mg m^{-3} .

The term $(M_i/M_T)(\bar{m}/m_i)$ is the approximate molar fraction of component i in the solvent mixture. Eq. (11) is equivalent to the original VBX model (Guo et al., 1998) but easier to use because it does not require any unit conversion between (mg m^{-3}) and (mole m^{-3}) for the concentration.

When the emission factor is estimated from the VOC contents in the formulation, it is more convenient to convert C_{v0} and C_{vi} to commonly used pressure units such as (mm Hg):

$$C_{v0} = 10^3 \frac{P_0 \bar{m}}{760 v_m}, \quad (12)$$

$$C_{vi} = 10^3 \frac{P_i m_i}{760 v_m}, \quad (13)$$

where P_0 = total vapor pressure for TVOCs, mm Hg;

P_i = vapor pressure for the pure component i , mm Hg; and

v_m = volume of 1 mole gas under 1 atm, m^3 ($v_m = 0.0243 \text{ m}^3$; at 23°C).

Substituting Eq. (12) into (10) and Eq. (13) into (11):

$$E = k_m \left(1.32 P_0 \frac{\bar{m}}{v_m} \frac{M_T}{M_{T0}} - C \right), \quad (14)$$

$$E_i = k_{mi} \left(1.32 P_i \frac{\bar{m}}{v_m} \frac{M_i}{M_T} - C_i \right). \quad (15)$$

The room concentration model consists of two differential equations for TVOCs (Eqs. (16) and (17)) and an additional two for each individual VOC (Eqs. (18) and (19)):

$$\frac{dC}{dt} = \frac{SE}{V} - NC, \quad (16)$$

$$\frac{dM_T}{dt} = -E, \quad (17)$$

$$\frac{dC_i}{dt} = \frac{SE_i}{V} - NC_i, \quad (18)$$

$$\frac{dM_i}{dt} = -E_i, \quad (19)$$

where E and E_i are from Eqs. (14) and (15), respectively. The most common initial conditions for Eqs. (16)–(19) are: $C = 0$, $C_i = 0$, $M_T = M_{T0}$, and $M_i = M_{i0}$ when $t = 0$. The amount of TVOCs and individual VOCs initially applied, M_{T0} and M_{i0} , can be calculated from:

$$M_{T0} = \theta dy_0, \quad (20)$$

$$M_{i0} = \theta dy_i, \quad (21)$$

where θ = wet film thickness, m,

d = product density, g m^{-3} ,

y_0 = TVOC content in the product, mg g^{-1} , and

y_i = content of component i in the product, mg g^{-1} .

Eqs. (20) and (21) are also valid when θ is in μm and d in kg l^{-1} .

This method requires knowledge of total vapor pressure (P_0) and average molecular weight (\bar{m}) for TVOCs,

and mass transfer coefficients (k_m and k_{mi}). Methods to estimate these parameters are described in Sections 4.2–4.4.

3.2. Method 2

In the second proposed method, the first-order decay model (Eq. 1) – the simplest possible source model for decaying sources – is adopted, with the two model parameters, E_0 and k , being estimated from the two mass transfer models described in the previous section by making certain approximations. At $t = 0$, Eqs. (14) and (15) become

$$E_0 = k_m \left(1.32 P_0 \frac{\bar{m}}{v_m} \frac{M_{T0}}{M_{T0}} - 0 \right) = 1.32 k_m P_0 \frac{\bar{m}}{v_m}, \quad (22)$$

$$\begin{aligned} E_{0i} &= k_{mi} \left(1.32 P_i \frac{\bar{m}}{v_m} \frac{M_{i0}}{M_{T0}} - 0 \right) \\ &= 1.32 k_{mi} P_i \frac{\bar{m}}{v_m} \frac{M_{i0}}{M_{T0}}, \end{aligned} \quad (23)$$

Since $M_{i0}/M_{T0} = y_i/y_0$, Eq. (23) can be changed to

$$E_{0i} = 1.32 k_{mi} P_i \frac{\bar{m}}{v_m} \frac{y_i}{y_0}. \quad (24)$$

From Eqs. (1) and (2), the first-order decay rate constant for TVOCs can be calculated from

$$k = \frac{E_0}{M_{T0}}. \quad (25)$$

Substituting Eq. (20) into Eq. (25)

$$k = \frac{E_0}{\theta dy_0}. \quad (26)$$

For an individual VOC, the decay rate constant (k_i) can be derived in a similar manner:

$$k_i = \frac{E_{0i}}{\theta dy_i}. \quad (27)$$

Once E_0 and k or E_{0i} and k_i are obtained, Eqs. (3) and (4) can be used to calculate room temperature concentrations.

4. Parameter estimation

4.1. Overview

The source models used in the two methods are summarized in Table 1. Table 2 is a list of all parameters required to compute indoor VOC concentrations with the two proposed methods: the first three parameters are properties of the environment, and the rest are properties of the source. It is fair to say that all the parameters can

Table 1
Summary of source models used in the proposed methods

Method	Category	Representation of solvent volatility	
		Vapor pressure (mm Hg)	Concentration at air-source Interface (mg m ⁻³)
1	TVOCs	$E = k_m \left(1.32 P_0 \frac{\bar{m}}{v_m} \frac{M_T}{M_{T0}} - C \right)$	$E = k_m \left(C_{v0} \frac{M_T}{M_{T0}} - C \right)$
	VOCs	$E_i = k_{mi} \left(1.32 P_i \frac{\bar{m}}{v_m} \frac{M_i}{M_T} - C_i \right)$	$E_i = k_{mi} \left(C_{vi} \frac{M_i \bar{m}}{M_T m_i} - C_i \right)$
2	TVOCs	$E_0 = 1.32 k_m P_0 \frac{\bar{m}}{v_m}$	$E_0 = k_m C_{v0}$
	VOCs	$E_{0i} = 1.32 k_{mi} P_i \frac{\bar{m}}{v_m} \frac{y_i}{y_0}$	$E_{0i} = k_{mi} C_{vi} \frac{y_i \bar{m}}{y_0 m_i}$

$$k = \frac{E_0}{\theta dy_0}$$

$$k_i = \frac{E_{0i}}{\theta dy_i}$$

Table 2
List of parameters required by the concentration models

Parameter	Symbol	Method 1		Method 2	
		TVOC	VOC	TVOC	VOC
Room volume	V	X	X	X	X
Air exchange rate	N	X	X	X	X
Mass transfer coefficient	k_m, k_{mi}	X	X	X	X
Source area	S	X	X	X	X
Wet film thickness	θ	X	X	X	X
Product density	d	X	X	X	X
Content of TVOC in product	y_0	X	X	X	X
Total vapor pressure for TVOC	P_0, C_{v0}	X	X	X	
Average molecular weight for TVOC	\bar{m}		X		X
Content of individual VOC in product	y_i		X		X
Vapor pressure for individual VOC	P_i, C_{vi}		X		X
Molecular weight for individual VOC	m_i		X		

be readily obtained except P_0 , \bar{m} , k_m and k_{mi} . Methods for estimating these parameters are discussed below.

4.2. Estimation of total vapor pressure for TVOC (P_0) from VOC contents in the product

To date, parameter P_0 can only be determined by experiment (an example is described below). An alternative method proposed here is to estimate P_0 based on the contents of major VOCs in the solvent. If we assume that the behavior of the solvent is close to an ideal solution, the total vapor pressure can then be estimated from Raoult's law. If the number of VOCs in the mixture is n , then

$$P_0 = \frac{\sum_{i=1}^n (P_i y_i / m_i)}{\sum_{i=1}^n (y_i / m_i)} \quad (28)$$

Although it is difficult to account for all the constituent VOCs in a petroleum-based solvent, routine chromatographic analysis of the coating material can easily identify one to two dozen major VOC peaks, which provides a good estimate of P_0 by using Eq. (28).

To estimate the accuracy of Eq. (28), the computed total vapor pressures were compared against those determined by headspace analysis for three test specimens: an alkyd primer, an alkyd paint, and a synthetic wood stain

Table 3
Comparison of headspace TVOC concentrations with theoretically calculated C_{v0} for three wet sources

Product	Measured C_{v0} (g m^{-3})	Computed		Percent Difference
		P_0 (mm Hg)	C_{v0} (g m^{-3})	
Alkyd Primer	27.2 ± 1.77	3.94	31.9	15.9
Alkyd Paint A	12.3 ± 1.66	1.44	14.3	15.0
Synthetic Stain	16.6 ± 1.91	2.86	18.4	10.3

^aMean \pm standard deviation; $n = 6$ for alkyd primer and alkyd paint; and $n = 7$ for synthetic stain.

(Tichenor *et al.*, 1993). About 120 ml of a paint sample was quickly poured into a 250 ml amber bottle, which was then sealed with a Teflon coated septum and placed in an incubator overnight at 23°C. A magnetic stirrer in the bottle helped mix the test specimen. For the synthetic wood stain, a 60 ml bottle was used and the volume of the test specimen was 20 ml. Samples (200–500 μl) were drawn from the headspace the next morning with a syringe which was heated to 60°C and rinsed once with the headspace air. The samples were then injected directly into a gas chromatograph/flame ionization detector (GC/FID) for quantitative analysis. The TVOC mass was computed by using the response factor for toluene and the sum of area counts between toluene and tetradecane, inclusive. In Table 3, the “measured” value was from the headspace analysis and the “computed” value from Eq. (28). The results showed that the difference between these two methods was no greater than 16%. We are uncertain, however, why the computed values are systematically greater than those from the headspace analysis.

Table 4 is an example demonstrating how P_0 can be calculated in an electronic spreadsheet. After entering VOC contents in the product, molecular weights and vapor pressures, the two sums in Eq. (28) are obtained. The total vapor pressure can then be calculated:

$$P_0 = \frac{2.348}{0.595} = 3.946 \text{ (mm Hg)} \quad (29)$$

4.3. Estimation of average molecular weight for TVOC (\bar{m}) from VOC contents in the product

We previously recommended that \bar{m} be represented by the molecular weight for the most predominant constituent in the solvent mixture (Guo *et al.*, 1998). In the majority of oil-based indoor coating materials we have tested, the most predominant VOC is either decane or undecane. An alternative method is to estimate \bar{m} based

Table 4

An exemplary worksheet for estimation of the total vapor pressure P_0 and average molecular weight (\bar{m}) for TVOCs

Compound	y_i	m_i	P_i^a	y_i/m_i	$P_i y_i/m_i$
Decane	30.7	142	1.575	0.2165	0.3410
Nonane	18.4	128	4.144	0.1436	0.5949
Octane	15.6	114	7.894	0.1372	1.0831
Undecane	6.68	156	0.616	0.0428	0.0264
trans-Decalin	2.28	138	3.296	0.0165	0.0543
2-Methyldecane	2.19	170	0.616	0.0129	0.0079
p-Xylene	1.39	106	7.710	0.0132	0.1014
Toluene	0.35	92	24.47	0.0038	0.0921
Ethylbenzene	0.29	106	8.850	0.0028	0.0246
o-Xylene	0.23	106	5.897	0.0022	0.0129
p-Ethyltoluene	0.21	120	2.864	0.0017	0.0050
1,2,4-Trimethylbenzene	0.14	120	2.028	0.0012	0.0024
Dodecane	0.063	170	0.253	0.0004	0.0001
n-Propylbenzene	0.034	120	3.126	0.0003	0.0009
1,3,5-Trimethylbenzene	0.023	120	2.526	0.0002	0.0005
Sum	78.6			0.595	2.348

^aAt 23 °C.

on the contents of major VOCs in the product:

$$\bar{m} = \frac{\sum_{i=1}^n y_i}{\sum_{i=1}^n (y_i/m_i)} \quad (30)$$

The calculations can be performed in the same spreadsheet for P_0 . No additional information is needed. In the example shown in Table 4, the calculated average molecular weight is

$$\bar{m} = \frac{78.6}{0.595} = 132 \text{ g mole}^{-1} \quad (31)$$

Parameter \bar{m} estimated from Eq. (30) is slightly smaller (less than 10% difference) than that represented by the most predominant VOC, which is decane in this example. We believe Eq. (30) is more accurate because more than half of the VOC constituents have smaller molecular weights than the most predominant constituent (see data in Table 4 for example).

4.4. Estimation of gas-phase mass transfer coefficients (k_m and k_{mi})

Parameters k_m and k_{mi} can be either determined by experiment or estimated based on gas-phase mass transfer theories. For experimental determination, the *p*-dichlorobenzene method (Guo et al., 1996) is commonly used.

Two theoretical models have been proposed to estimate gas-phase mass transfer coefficients in indoor environments (Sparks et al., 1996; Zhang et al., 1996). The model proposed by Sparks et al. – the simpler one of the two – is derived by finding the correlation between the

Nusselt number (Nu) and the Reynolds number (Re) from experimental data:

$$\text{Nu} = 0.33 \text{ Re}^{2/3} \quad (r^2 = 0.98, n = 24) \quad (32)$$

and the equation used to compute the mass transfer coefficient is

$$k_m = 0.33 D L_c^{-1/3} \left(\frac{v \rho}{\mu} \right)^{2/3} \quad (33)$$

where D = diffusivity of the VOC in air, $\text{m}^2 \text{h}^{-1}$,
 L_c = characteristic length of the source (equal to the square root of the source area), m,
 v = air velocity over the source, m h^{-1} ;
 ρ = density of the air, g m^{-3} ; and
 μ = viscosity of the air, $\text{g h}^{-1} \text{m}^{-1}$.

In general, all the parameters in Eq. (33) can be obtained readily. The density and viscosity of the air can be found from the literature. Parameters L_c and v vary from case to case. Fig. 1 shows the mass transfer coefficient as a function of air velocity and characteristic length for decane ($D = 0.0207 \text{ m}^2 \text{h}^{-1}$). An air velocity range of $5\text{--}10 \text{ cm s}^{-1}$ is considered typical in indoor environments (Mathews et al., 1987).

The following is an example of how the mass transfer coefficient is estimated for decane emissions from a surface with an area of 12 m^2 when the indoor temperature is 23°C and air velocity 10 cm s^{-1} . The values needed to compute k_m are

$$L_c = \sqrt{12} = 3.466 \text{ m}, \quad (34)$$

$$v = 10 \text{ cm s}^{-1} = 360 \text{ m h}^{-1}, \quad (35)$$

$$D = 0.0576 \text{ cm}^2 \text{ s}^{-1} = 0.0207 \text{ m}^2 \text{ h}^{-1}, \quad (36)$$

$$\rho = 1193 \text{ g m}^{-3}, \quad (37)$$

$$\mu = 184.4 \text{ } \mu \text{ poises} = 66.52 \text{ g h}^{-1} \text{ m}^{-1}, \quad (38)$$

where ρ and μ were found from the literature (Weast, 1972) and D was calculated by using the FSG method (Layman et al., 1982). Substituting the above values into Eq. (33) yields:

$$k_m = 0.33 \times 0.0207 \times (3.464)^{-1/3} \left(\frac{360 \times 1193}{66.52} \right)^{2/3} \\ = 1.57 \text{ m h}^{-1}. \quad (39)$$

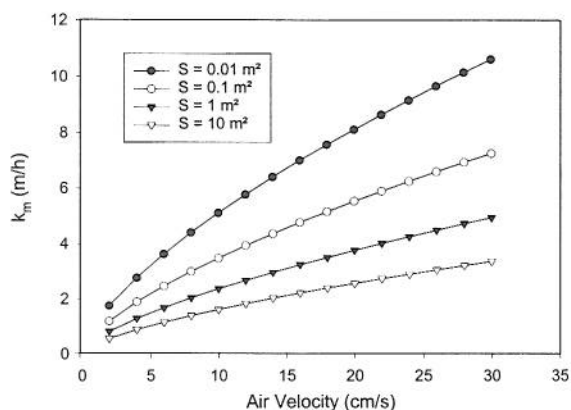


Fig. 1. Gas-phase mass transfer coefficient (k_m) as a function of air velocity and source area (S).

Table 5
Summary of test specimens and chamber conditions^a

Test specimen	Alkyd Primer	Alkyd Paint B	Conversion varnish
Product density (kg l^{-1})	1.33	1.10	0.97
TVOC content (mg g^{-1})	333	350	516
Most abundant VOC	Decane	Decane	Xylene
No. of VOCs quantified in liquid product	20	20	10
No. of VOCs quantified in air samples	20	20	4
Total vapor pressure (mm Hg) ^b	3.94	2.58	8.39
Average molecular weight ^c	131	133	101
Substrate type	White pine board	White pine board	Red oak board
Substrate area (cm^2)	256	256	272
Recommended wet film thickness (μm)	102	102	76–102
Actual wet film thickness (μm)	82.5	74.6	123
Air exchange rate (h^{-1})	0.543	0.543	0.538
Mass transfer coefficient (m h^{-1}) ^d	4.36	4.36	4.36

^aAll three tests were conducted in 53 l stainless steel chambers at 23 °C and 50% relative humidity.

^bEstimated from Eq. (28).

^cEstimated from Eq. (30).

^dFor decane; estimated from Eq. (33).

Practically, the mass transfer coefficient for TVOC is represented by that for the most abundant component (Tichenor et al., 1993).

5. Evaluation of model performances

5.1. Chamber data

Small chamber data for three types of indoor coating materials were used to evaluate the performance of the proposed methods: an alkyd primer, an alkyd paint, and a conversion varnish that cures at room temperature. The solvents used in the first two products were typical petroleum distillate solvents. The conversion varnish contains large amount of aromatic compounds. Table 5 summarizes the properties of the test specimens and the test conditions. Detailed information about these products and test procedures are reported elsewhere (Fortmann et al., 1998; Howard et al., 1998). Not all concentration data were used in this evaluation. Data for some VOCs were disqualified for one or more of the following reasons: (1) most data points were below the practical method quantification limit; (2) the chamber recovery was either less than 75% or greater than 125% and (3) the vapor pressure for a given VOC was not available at room temperature range. Thus, only 23 sets of concentration data were qualified for the evaluation.

5.2. Results

The performance of the two methods was evaluated by using two indicators: the error in the predicted peak

Table 6
Comparison of observed and predicted peak concentrations in mg m^{-3}

Test specimen	Compound	Observed	Method 1		Method 2	
			Predicted	% Diff. ^a	Predicted	% Diff. ^a
Alkyd Primer	TVOCs	9.77×10^3	8.91×10^3	− 9.3	1.23×10^4	+ 22
	Decane	1.10×10^3	8.76×10^2	− 23	8.92×10^2	− 21
	Nonane	6.63×10^2	6.71×10^2	+ 1.2	7.01×10^2	+ 5.6
	<i>trans</i> -Decalin	6.76×10^1	7.93×10^1	+ 16	8.19×10^1	+ 19
	<i>p</i> -Xylene	4.26×10^1	5.65×10^1	+ 28	5.94×10^1	+ 33
	Ethylbenzene	1.17×10^1	1.21×10^1	+ 3.4	1.28×10^1	+ 9.0
	<i>o</i> -Xylene	8.31×10^0	9.12×10^0	+ 9.3	9.89×10^0	+ 17
	<i>p</i> -Ethyltoluene	6.19×10^0	7.06×10^0	+ 13	7.29×10^0	+ 16
Alkyd Paint B	TVOCs	6.55×10^3	6.36×10^3	− 2.9	9.32×10^3	+ 35
	Decane	4.62×10^2	4.87×10^2	+ 5.3	5.45×10^2	+ 16
	Undecane	4.01×10^2	4.60×10^2	+ 14	5.28×10^2	+ 27
	Nonane	1.92×10^2	2.05×10^2	+ 6.5	2.23×10^2	+ 15
	<i>trans</i> -Decalin	7.37×10^1	1.16×10^2	+ 45	1.29×10^2	+ 55
	Methylethylketoxime	7.01×10^1	5.97×10^1	− 16	6.69×10^1	− 4.7
	<i>p</i> -Ethyltoluene	3.45×10^1	3.82×10^1	+ 10	4.19×10^1	+ 19
	<i>o</i> -Xylene	3.01×10^1	4.09×10^1	+ 30	5.48×10^1	+ 58
	1,2,4-Trimethylbenzene	1.55×10^1	2.55×10^1	+ 49	2.54×10^1	+ 48
	<i>n</i> -Propylbenzene	7.72×10^0	1.07×10^1	+ 32	1.18×10^1	+ 42
Conversion Varnish	Isopropylbenzene	3.79×10^0	4.86×10^0	+ 25	5.31×10^0	+ 33
	<i>p</i> -xylene	9.78×10^3	9.11×10^3	− 7.0	1.00×10^4	+ 2.3
	Isobutanol	3.48×10^3	3.85×10^3	+ 9.9	3.65×10^3	+ 4.7
	<i>o</i> -Xylene	2.79×10^3	2.26×10^3	− 21	2.41×10^3	− 15
Ethylbenzene		2.31×10^3	2.18×10^3	− 5.9	2.49×10^3	+ 7.3
Average percent difference ^b				16.6		22.9

^aPercent difference.

^bAverage of absolute values.

concentration and the normalized mean square error (NMSE) for a given data set. As shown in Table 6, the average percent difference between observed and predicted peak concentrations is 16.6% for method 1 and 22.9% for method 2. The observed peak concentrations cover a wide range (from 3.79 to 9780 mg m^{-3}) and, thus, the two methods work for both major and minor components of the solvent mixture. It should be pointed out, however, that the predicted peak concentrations are often (but not always) higher than the observed ones. Possible causes of such overestimation are discussed in the following section.

The NMSE, one of the standard indices for statistical evaluation of indoor air quality models (ASTM, 1995b), is calculated from

$$\text{NMSE} = \frac{\sum_{i=1}^n (C_{pi} - C_{oi})^2}{n \bar{C}_o \bar{C}_p}, \quad (40)$$

where C_{pi} = predicted concentrations,

C_{oi} = observed concentrations,

$$\bar{C}_o = \sum_{i=1}^n C_{oi}/n,$$

$$\bar{C}_p = \sum_{i=1}^n C_{pi}/n, \text{ and}$$

n = total number of data points.

As shown in Table 7, the average NMSE value was 0.159 for method 1 and 0.253 for method 2. According to the ASTM standard guide, an NMSE value of 0.25 or less is generally considered indicative of adequate model performance.

Both indicators suggest that the performances of the two methods are adequate and that, in general, method 1 is more accurate than method 2. Examples of predicted chamber concentrations with good and poor accuracy are shown in Figs. 2 and 3, respectively.

6. Discussion

6.1. Comparison of the two methods

Each of the two proposed methods has its advantages and disadvantages. The first method provides more accurate predictions and is less sensitive to errors in the input.

Table 7
Normalized mean square error (NMSE) as an indicator of model accuracy

Test specimen	Compound	Method 1	Method 2
Alkyd Primer	TVOC	0.067	0.044
	Decane	0.097	0.106
	Nonane	0.024	0.045
	<i>trans</i> -Decalin	0.229	0.212
	<i>p</i> -Xylene	0.236	0.293
	Ethylbenzene	0.032	0.056
	<i>o</i> -Xylene	0.036	0.057
	<i>p</i> -Ethyltoluene	0.459	0.633
Alkyd Paint B	TVOC	0.116	0.389
	Decane	0.111	0.147
	Undecane	0.125	0.169
	Nonane	0.160	0.218
	<i>trans</i> -Decalin	0.542	0.687
	Methylethylketoxime	0.204	0.240
	<i>p</i> -Ethyltoluene	0.117	0.168
	<i>o</i> -Xylene	0.377	0.547
	1,2,4-Trimethylbenzene	0.508	0.470
	<i>n</i> -Propylbenzene	0.384	0.522
	Isopropylbenzene	0.375	0.498
Conversion	Ethylbenzene	0.059	0.064
Varnish	<i>o</i> -Xylene	0.116	0.111
	Isobutanol	0.054	0.068
	<i>p</i> -Xylene	0.048	0.070
Average NMSE		0.195	0.253

On the other hand, this method requires solving a system of differential equations numerically and, therefore, is relatively computation intensive.

The second method is less accurate but easier to use. All the calculations can be performed in an electronic spreadsheet. Thus, it is more suitable for product screening purposes. It is also of choice if a large number of calculations are needed (such as in Monte Carlo analysis).

In terms of computational intensity, the difference between these two methods is more significant for individual VOCs than for TVOCs. The reader is reminded that, in a single-zone situation, the VB model has an explicit solution to indoor concentration (Tichenor et al., 1993). With slightly more computational steps, this mass transfer model offers better accuracy than the first-order decay model.

6.2. Validity of estimating total vapor pressure for TVOCs from the VOC contents in the product

Because of the many constituent VOCs contained in the petroleum-based solvent, the predominant VOCs

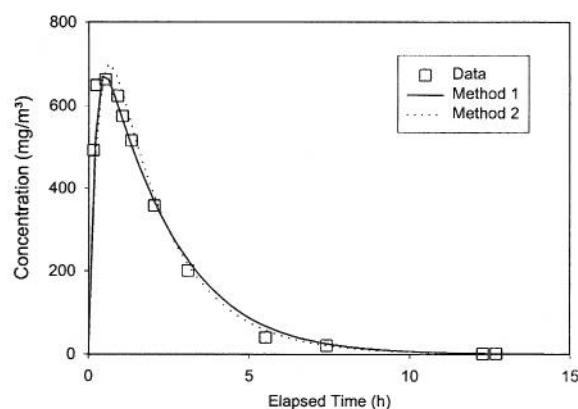


Fig. 2. An example of model predictions with good accuracy. NMSE = 0.024 for method 1 and 0.045 for method 2. Data are for nonane in the alkyd primer test.

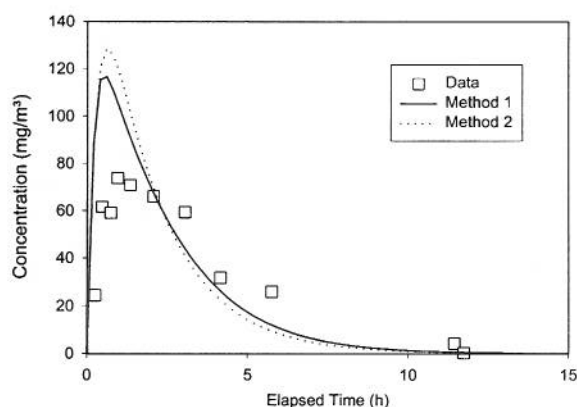


Fig. 3. An example of model predictions with poor accuracy. NMSE = 0.542 for method 1 and 0.687 for method 2. Data are for *trans*-decalin in the alkyd paint test.

that can be quantified by routine GC analysis account for only a small portion of the total mass. In the example shown in Table 4, the 15 quantified major VOCs account for about 24% of the total weight of the solvent (the TVOC content was 333 mg g^{-1}). It is doubtful that 24% of predominant VOCs can represent the properties of the solvent if there is no similarity between those components and the remaining 76% of the VOCs. As stated in Introduction, above, petroleum-based solvents consist mainly of aliphatic hydrocarbons. Although many less abundant constituents are not the targets in routine GC analysis, their properties are similar to some of the quantified VOCs. For instance, *n*-decane is the most abundant component in many solvent-based coating products. This compound also has many isomers (e.g., branched decanes), which are not quantified but have molecular weights and diffusivities identical to *n*-decane and vapor

pressures close to *n*-decane. Thus, *n*-decane represents a group of VOCs with similar physical properties. The usefulness of Eq. (28) is that it makes the headspace analysis unnecessary.

6.3. Overestimation of peak concentrations

As shown in Table 6, both methods tend to overestimate the peak concentrations. There are several explanations for the causes. First of all, the test specimen was prepared outside the chamber and it typically took several minutes to apply the coating and to determine the total amount of material applied. Such a delay may cause significant VOC loss before the test specimen is placed in the chamber, especially for more volatile components (Guo et al., 1996).

The second cause is the substrate effect. When a petroleum-based coating material is applied to a substrate such as wood or gypsum boards, a small amount of solvent will penetrate the substrate. This fraction of solvent will be emitted in a delayed time. Limited data analysis suggests that this fraction accounts for 5–10% of the total solvent applied.

The third cause applies only to the second method. It is due to the omission of the back pressure effect. As shown in Eqs (10) and (11), the driving force for solvent evaporation is the concentration difference between the surface of the source and the indoor air. As a result, the high chamber concentration in the early hours slows the evaporation process. Method 2 does not take this factor into consideration and, consequently, its predicted peak concentrations are generally higher than those predicted by method 1.

6.4. Making use of information in material safety data sheets and product data sheets

Predicting the emission rate of an individual VOC with the first-order decay model does not require knowledge of the total vapor pressure for TVOCs (Eqs. (24) and (27)). This feature makes it possible to estimate the emission rate based on the information in the Material Safety Data Sheets (MSDSs) and the Product Data Sheets. The United States laws require that the manufacturer provide MSDSs with their products. For indoor coating products, the contents of total volatile matter (TVM) and some hazardous VOCs (> 1% by weight) are reported in MSDSs. If the VOC of interest appears in the MSDS, one can use Eqs. (24) and (27) to roughly estimate its emission rate. The TVOC content can be represented by TVM. The only information lacking about the TVOCs is their average molecular weight. In most indoor coating products we have tested, including wood stain, polyurethane wood finish, floor wax and alkyd paint (Tichenor et al., 1991, 1993; Fortmann et al., 1998), the most predominant VOC in the solvent is either

decane ($m_i = 142$) or undecane ($m_i = 156$). The only exception was conversion varnish, in which xylene ($m_i = 106$) is often the most abundant component in the solvent (Howard et al., 1998). For screening purposes, we recommend that the average molecular weight of 142 be used when the most abundant component is unknown. The density of the product is always reported in the related Product Data Sheet.

7. Conclusions

Two methods have been developed to predict the emissions of TVOCs and individual VOCs from solvent-based indoor coating materials based on the product formulation. The first method is based on two mass transfer models with the key parameters being estimated from the contents of major VOCs in the product. The second method utilizes the first-order decay model with its parameters being estimated based on the properties of the source and the environment. Model evaluation using small chamber data indicates that both methods provide reasonable accuracy in predicting emissions to indoor environments, with the average normalized mean square error being 0.159 and 0.253, respectively. Further evaluation with data collected from real rooms, where VOC adsorption and desorption from interior surface are often significant, is desirable.

The first method is more accurate than the second but is more computation intensive. The second method is simple enough to be implemented in an electronic spreadsheet and is more suitable for product screening. These two methods provide a way to obtain exposure information on the indoor use of petroleum-based indoor coating materials without having to perform costly chamber testing.

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