

Measurements of Volatile Organic Compound (VOC) Emissions from Wood Stains Using an Electronic Balance

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ABSTRACT

An emissions test method using an electronic balance is introduced for measuring the TVOC emission rates of oil-based wood stains, with a detailed procedure for preparing test specimens. The emission characteristics of volatile organic compounds (VOC) from an artificial wood stain and an oil-based commercial wood stain were determined. Results showed that VOC emissions from both stains included a surface evaporation and an internal diffusion sub-process. With regard to time, the entire emission period could be divided into three periods: (1) an initial evaporation-controlled period that was characterized by a high and fast decaying emission rate, (2) a transition period (following the initial period) in which the emissions transitioned from an evaporation-controlled to an internal diffusion-controlled process, and (3) an internal diffusion-controlled period that was characterized by a low and slowly decaying emission rate. For the commercial wood stain tested, the length of the initial period was approximately three hours, and about 46% of the emittable VOC mass was emitted during this short period. The transition period was between 3 and 6.5 hours from the start of testing and only accounted for about 4% of VOC mass emitted. The rest (about 50%) of the VOC mass was emitted in the diffusion-controlled period over a long period of time. Comparison between the commercial wood stain and an artificial wood stain suggested that the pigments/solids in the wood stain had significant effect on the time scales and amount of mass emitted during each emission period. The presence of additional VOCs in the commercial wood stain might have also affected the emission profiles. These results are useful for developing better models for predicting the emission rates. The electronic balance method was also compared with those determined

from the TVOC concentrations measured at the chamber exhaust (referred to as "chamber method"). Results show that the two methods agreed well with each other, confirming the validity of the complete mixing assumption that is often used in environmental chamber testing. These results are useful for developing standard test protocols for testing "wet" building materials such as wood stains, varnishes, and paints.

INTRODUCTION

Data on the emissions of volatile organic compounds (VOCs) from building materials are needed to assess the impact of building material off-gassing on the indoor air quality of buildings. This study deals with the emissions of "wet" coating materials such as wood stains, varnishes, and paints. These materials are wet when they are applied onto a substrate and gradually dry from the surface down. Because of the phase change associated with the drying process, the emission characteristics of these materials are affected by both the substrate and the application method. A standardized procedure for preparing the substrate and applying the test specimen is necessary to obtain repeatable results.

Using small environmental chambers, previous studies have indicated that the emission process of "wet" materials appears to consist of two periods: (1) an initial period with a high and fast decaying emission rate, which is primarily controlled by the evaporative mass transfer; (2) a second period with a low and slowly decaying emission rate, which is primarily controlled by the internal diffusion of VOC through the substrate surface (see Chang and Guo 1992; Wilkes et al. 1996; Zhang et al. 1996a). Much progress has also been made in developing mass transfer models for the evaporation-controlled period. Guo and Tichenor (1992) developed an

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evaporative mass transfer model for TVOC emission from interior architectural coatings. Spark et al. (1996) discussed the application of gas-phase mass transfer models for indoor pollutant sources. Guo et al. (1998) further developed a mass transfer model for predicting the emission rates of individual VOCs from petroleum-based indoor coatings. However, progress in modeling the internal diffusion-controlled emission period is limited, partly due to the lack of experimental data. Chang et al. (1997) found that substrate significantly affected the emission rates and patterns of VOCs from a latex paint. The substrate effect makes it more difficult to model the internal diffusion-controlled emission period for "wet" coating materials.

In this study, a test method using an electronic balance was introduced, which enables a more direct measurement of the total VOC emission rate than the environmental chamber testing method. The objectives of the present study were to (1) provide experimental data for a better understanding of the emission characteristics of wood stains that are applied on a realistic substrate and to (2) develop and evaluate a method for preparing test specimens. The results are useful for developing better mathematical models for predicting emission rates and for developing standard emission testing methods and procedures for "wet" coating materials such as wood stains, paints, varnishes, etc.

EXPERIMENTAL

Consideration

Both a commercial wood stain and an artificial wood stain (a mixture of five pure VOC compounds containing the major compounds in the commercial wood stain) were tested in this study. Because the artificial wood stain contained no additives, all its mass applied was expected to be emitted from the substrate. Thus, it was possible to use the same substrate for subsequent tests to eliminate the substrate effect. It also provided reference data for comparison with the emission characteristics of the commercial wood stain so that the effect of the pigments in the wood stain on the emission rate could be identified. A total of five tests were conducted on the artificial wood stain, and three pieces of oak boards were used as the substrates. Two of these substrates were each used twice.

For the commercial wood stain, a total of nine repeat tests were conducted. A different piece of oak board was used as the substrate for each test. The purpose of conducting the repeat tests was to allow quantification of the experimental uncertainty as well as the emission characteristics of the wood stain.

Testing Facility and Conditions

Experiments were conducted in a full-scale (5 m × 4 m × 2.75 m high, 55 m³ in volume) environmental chamber (Zhang et al. 1996b). The chamber was operated under a full exhaust mode (i.e., no recirculated air) with the following conditions:

Supply airflow rate: 2.5 ACH, equivalent to

8.23 L/s (81 ft³/min)

Return/exhaust air temperature: 23 ± 0.5°C

Return/exhaust air relative humidity: 50% ± 2% RH

The supply air was well mixed with the air in the chamber as verified previously (Zhang et al. 1996b). The temperature and relative humidity measured at the return air duct were representative of the average conditions in the chamber and were used as the reference for controlling the conditions in the chamber.

An electronic balance was used to monitor the weight loss due to the VOC emissions from the test wood stains. The resolution of the electronic balance was 1.0 mg. The weight of the wood stain/substrate specimen was measured every 10 seconds during the first 15 minutes. The measurement frequency was reduced to every 30 seconds between the 15th and 60th minute, and every 1 minute after 60 minutes of the test. Data were recorded by a microcomputer that was connected to the electronic balance via a RS232 communication cable. Figure 1 shows a schematic of the experimental setup.

The electronic balance was located at a corner of the chamber so that the supply air would not blow directly on the test specimen. The local air velocity, measured by a hot wire anemometer at 10 mm above the specimen surface, was approximately 0.03 ± 0.01 m/s (about 6 ft/min). For the commercial wood stain tests, in order to compare the results between the electronic balance test method and the conventional chamber test method, the TVOC concentrations were also measured by using a gas monitor at several locations, including the return/exhaust air duct and the center and corner of the full-scale chamber (Figure 1) at six-minute intervals. The gas monitor was calibrated by using cyclohexane (C₆H₁₂) as the reference gas.

Testing Materials

Two material samples were used for this study: an oil-based commercial wood stain and an artificial "wood stain." The commercial wood stain was purchased from a local store. It has four major compounds, identified in a previous study for this product (Zhang et al. 1996a): nonane, decane, undecane, and dodecane. To estimate the total emittable VOC content in the wood stain, a small amount of wood stain was applied onto a glass plate and its weight loss was monitored over a period of 454 hours (about 19 days) at 23 ± 1°C and approximately 1 atmospheric pressure. The results of three such tests are listed in Table 1, which indicates that the emittable VOC content was approximately 73.25% ± 0.54% of the initial wood stain mass, assuming that all the weight loss was due to the VOC emissions.

The artificial wood stain was a mixture of five pure compounds including: n-octane, n-nonane, n-decane, n-undecane, and n-dodecane. The properties of these compounds and their fractions in the mixture are listed in Table 2. Because the artificial wood stain does not contain any additives, it was expected that the total emittable mass of the artificial wood

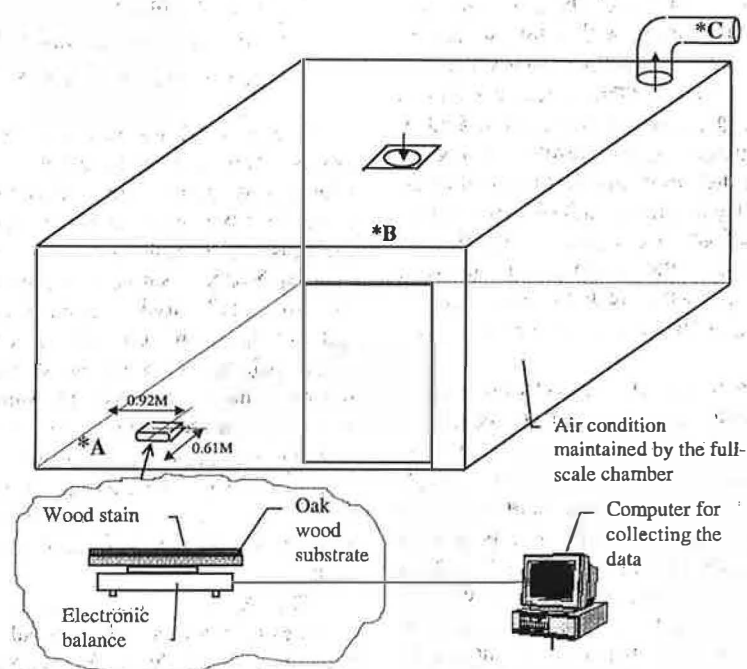


Figure 1 Schematic of the experimental setup. Gas monitor sampling locations: A—corner, B—center, and C—return/exhaust air duct.

TABLE 1

Percentage Ratio (%) Between the Weight Loss and Initial Weight of Wood Stains Applied on Glass Substrate

Elapsed time (hour)	Test 1 (W ₀ = 0.329 g)	Test 2 (W ₀ = 0.335 g)	Test 3 (W ₀ = 0.114 g)	Mean	Std.
0.33	48.632	49.851	56.140	51.541	4.029
0.85	67.477	64.776	69.298	67.184	2.275
120.17	72.644	73.134	73.684	73.154	0.520
138.33	72.644	73.134	73.684	73.154	0.520
162.53	72.644	73.134	73.684	73.154	0.520
454.02	72.644	73.433	73.684	73.254	0.543

* Weight loss = initial weight - weight at the time of measurement.

TABLE 2

Properties of the Mixture Compounds and their Molar Fractions in the Artificial Wood Stain

Compound	Formula	M.W.	Vapor Pressure (mm Hg)	Molar Fraction	Weight Fraction (%)
n-Octane	C ₈ H ₁₈	114	12.07	0.1	8.03
n-Nonane	C ₉ H ₂₀	128	3.93	0.2	18.03
n-Decane	C ₁₀ H ₂₂	142	1.25	0.4	40.00
n-Undecane	C ₁₁ H ₂₄	156	0.35	0.2	21.97
n-Dodecane	C ₁₂ H ₂₆	170	0.12	0.1	11.97

* 23°C (from VOCBASE 1996).

stain would be 100% of the initial mass under the test conditions (23°C and 50% RH).

Testing Procedure

For each test, the oak wood substrate (250 mm × 240 mm × 10 mm thick) was first conditioned in the full-scale chamber until its temperature and moisture conditions were in equilibrium with the ambient air as indicated by a constant reading of the electronic balance, indicating that there was no more moisture loss or gain (which took at least 72 hours). During this period, it was found that the reading of the electronic balance was very sensitive to the relative humidity fluctuation in the chamber. The control system of the chamber was, therefore, improved to reduce humidity fluctuation to less than ±2% RH (note that the precision requirement for most standard environmental chamber tests is ±5% RH).

The commercial or artificial wood stain was then applied onto the substrate outside the chamber. Appendix A describes a detailed procedure for preparing test specimens, which was developed after trying several different techniques. The specimen was then placed on the electronic balance. The whole process took approximately two to three minutes to complete. The time when the test specimen was placed on the balance was defined as "Time Zero."

RESULTS AND DISCUSSIONS

Measured Weight Loss

Figures 2 and 3 show the measured weight decay for the artificial wood stain and commercial wood stain, respectively. The curves in Figures 2 and 3 indicate that the weight of both artificial and commercial wood stains decreased very fast initially, but the rate of decrease slowed down with time. The measured weight became relatively stable after a certain period of time.

For the artificial wood stain, Test A1b was a duplicate of Test A1a, using the same piece of oak board as the substrate, and Test A2b was a duplicate of Test A2a. Figure 2 shows that tests conducted with the same piece of oak board (Tests A1a and A1b, Tests A2a and A2b) gave very similar results. This suggests that the procedure used for applying the wood stain was able to provide very consistent results on the normalized weight loss despite the small difference in the amount of mass applied. It also suggests that the variation in the substrate materials may be mainly responsible for the variation in the results shown in Figure 2 (between Tests A1, A2, and A3) and Figure 3.

To facilitate further data analysis, the following double exponential equation was used to describe the measured weight data:

$$w(t) = a \exp(-k_1 t) + b \exp(-k_2 t) \quad (1)$$

where

$w(t)$ = weight of wood stains remaining on the specimen board, mg;

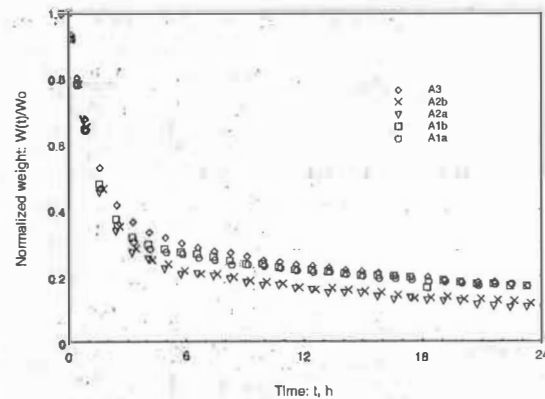


Figure 2 Measured weight decay data for the artificial wood stain. Plotted every 50 measured points; see Table 3 for values of W_0 .

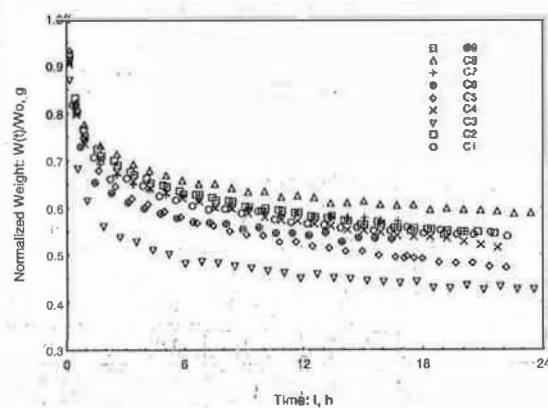


Figure 3 Measured weight decay data for the commercial wood stain. Plotted every 50 measured points; see Table 4 for values of W_0 .

a, b, k_1, k_2 = constants whose values are determined by the method of least squares regression analysis. It will be seen later that ak_1 and ak_2 correspond to the initial emission rates of the first and second exponential decay processes, respectively.

Tables 3 and 4 list the regression analysis results. The coefficient of determination (R^2) was higher than 0.98, indicating that the measured weight decay data can be very well represented by Equation 1.

Emission Rates and Emission Periods

Assuming that the weight loss is equal to the amount of volatile organic compound (VOC) mass emitted from the wood stains, the emission rate can be calculated by

$$E(t) = -d[w(t)]/dt = a k_1 \exp(-k_1 t) + b k_2 \exp(-k_2 t). \quad (2)$$

TABLE 3
Regression Results on Measured $w(t)$ for Artificial Wood Stain Using the Double Exponential Model*

Test ID	A1a	A1b	A2a	A2b	A3	Mean	RSD, %†
Wo, g	3.931	3.744	4.782	4.392	4.062	4.182	9.810
a	2.792	2.607	3.110	3.337	3.009	2.971	9.516
b	1.135	1.136	1.640	1.082	1.048	1.208	20.224
k_1	0.805	0.845	0.738	0.675	0.791	0.771	8.549
k_2	0.024	0.026	0.031	0.032	0.039	0.030	18.920
R^2	1.000	1.000	1.000	1.000	0.999	1.000	0.009
$(a k_1)/(b k_2)$	82.456	74.709	44.624	64.910	58.703	65.080	22.449
k_1/k_2	33.513	32.556	23.527	21.039	20.438	26.215	24.191
t_1 , h	5.65	5.26	5.38	6.49	5.42	5.64	8.79
t_2 , h	11.54	10.88	11.89	13.65	11.54	11.90	8.76
M_1/M_T , %	73.94	72.69	69.13	79.67	77.94	74.67	5.63
M_2/M_T , %	78.01	77.09	75.72	84.72	83.37	79.98	5.02
$(M_2-M_1)/M_T$, %	4.07	4.40	6.58	5.05	5.42	5.11	19.18

* Emitting surface area: $A = 0.060 \text{ m}^2$ for all tests; total emittable mass: $M_T = W_o$.

† Relative standard deviation: ratio between the standard deviation and the mean value.

TABLE 4
Results of the Regression Analysis on $w(t)$ for Commercial Wood Stain Using the Double Exponential Model*

Test ID	C1	C2	C3	C4	C5	C6	C7	C8	C9	Mean	RSD, %†
Wo, g	4.360	4.711	3.910	4.846	4.411	3.667	4.046	4.340	4.212	4.278	8.69
a	1.453	1.379	1.759	1.400	1.509	1.253	1.283	1.178	1.219	1.382	12.98
b	2.797	3.210	2.068	3.248	2.853	2.282	2.676	2.997	2.882	2.779	14.12
k_1	1.026	1.177	1.661	1.373	1.314	1.574	1.452	1.213	1.464	1.362	14.80
k_2	0.009	0.012	0.010	0.013	0.017	0.011	0.010	0.008	0.012	0.011	24.99
R^2	0.998	0.998	0.998	0.998	0.999	0.999	0.999	0.998	0.999	0.998	0.04
$(a k_1)/(b k_2)$	61.214	43.675	134.938	47.081	40.003	82.312	71.594	61.931	51.558	66.034	44.25
k_1/k_2	117.854	101.688	158.675	109.225	75.602	149.604	149.289	157.523	121.918	126.820	22.74
t_1 , h	4.04	3.24	2.97	2.83	2.84	2.82	2.96	3.42	2.72	3.09	13.59
t_2 , h	8.57	7.19	5.76	6.21	6.40	5.77	6.15	7.24	5.89	6.58	14.17
M_1/M_T , %	47.79	31.13	46.28	30.64	36.52	35.65	33.17	28.52	30.58	46.64	15.43
M_2/M_T , %	51.77	34.70	48.07	33.92	41.01	37.89	35.56	30.90	33.60	50.60	13.69
$(M_2-M_1)/M_T$, %	3.98	4.88	2.45	4.48	6.13	3.06	3.27	3.24	4.11	3.96	28.17

* Emitting surface area: $A = 0.060 \text{ m}^2$ for all tests; total emittable mass: $M_T = 0.73254 W_o$ (Table 1).

† Relative standard deviation: ratio between the standard deviation and the mean value.

Equation 2 is identical to the double exponential model proposed by Colombo et al. (1991) for describing the VOC emission rates measured in small environmental test chambers.

Equation 2 assumes that VOC emissions from wood stains may consist of two first-order decay processes. That is,

$$E(t) = E_1(t) + E_2(t), \quad (3)$$

$$E_1(t) = E_1(0) \exp(-k_1 t), \quad (4)$$

$$E_2(t) = E_2(0) \exp(-k_2 t), \quad (5)$$

where

$E_1(0) = a k_1$, representing the initial emission rate of the first exponential decay process with k_1 being the decay constant;

$E_2(0) = b k_2$, representing the initial emission rate of the second exponential decay process with k_2 being the decay constant.

As shown in Tables 3 and 4, for both the artificial and commercial wood stains, Equation 2 has the following characteristics:

$$a k_1 \gg b k_2 \text{ and } k_1 \gg k_2.$$

This means that $E_1(t)$ represents an emission process with a high initial emission rate and a fast decay rate (i.e., large decay constant), while $E_2(t)$ represents an emission process with a low initial emission rate and a slow decay rate (i.e., small decay constant). As wood stains are supposed to penetrate the material to which they are applied for protection, it is postulated that as soon as a wood stain is applied on a substrate, some of the wood stain will penetrate into the substrate, carrying with it some of the VOCs. The VOCs in the wood stain on the surface will evaporate at a high initial emission rate as it dries up. As the amount of VOCs on the surface decreases and as the stain gradually dries up, the emission rate decreases quickly. This corresponds to the first portion of the VOCs emitted, whose emission rate is controlled by evaporation and is represented by $E_1(t)$. The second portion of the VOCs include those initially penetrated into the substrate and those absorbed in the pigments (in the case of the commercial wood stain). The second portion of VOCs need to diffuse to the surface before they are evaporated into the air, and, therefore, their emission rate is primarily controlled by internal diffusion through the substrate and/or pigments, resulting in a low and slowly decaying emission rate as represented by $E_2(t)$.

We propose to define two time scales, t_1 and t_2 , at which

$$E_1(t_1) = E_2(t_1) \quad (6)$$

and

$$E_1(t_2) / E_2(t_2) = 1\%. \quad (7)$$

Using Equations 4 and 5 in Equations 6 and 7, respectively, it can be derived that

$$t_1 = 1/(k_1 - k_2) \ln(a k_1)/(b k_2) \quad (8)$$

and

$$t_2 = 1/(k_1 - k_2) \ln(100 a k_1)/(b k_2). \quad (9)$$

The VOC mass emitted from time 0 to time t_1 and from time 0 to t_2 can be calculated by Equations 10 and 11, respectively.

$$M_1 = a [1 - \exp(-k_1 t_1)] + b [1 - \exp(-k_2 t_1)] \quad (10)$$

$$M_2 = a [1 - \exp(-k_1 t_2)] + b [1 - \exp(-k_2 t_2)] \quad (11)$$

The values of t_1 , t_2 , M_1 , and M_2 for each tests are listed in Tables 3 and 4 for the artificial and commercial wood stains, respectively. Figure 4 shows the mean values of t_1 and t_2 for a normalized emission rate, $E(t)/E(0)$, vs. time curve, and

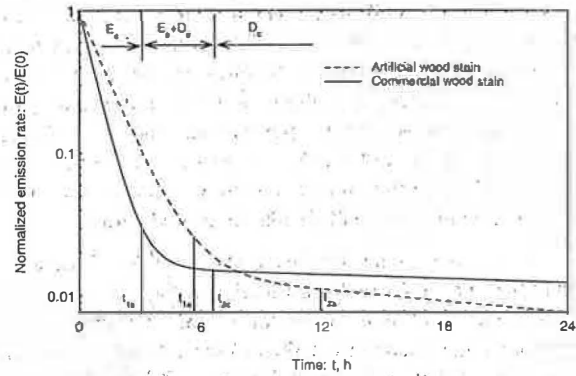


Figure 4 Normalized emission rate vs. time. E_c , $E_c + D_c$ and D_c represent evaporative-controlled, transition, and diffusion-controlled periods for commercial wood stain, respectively.

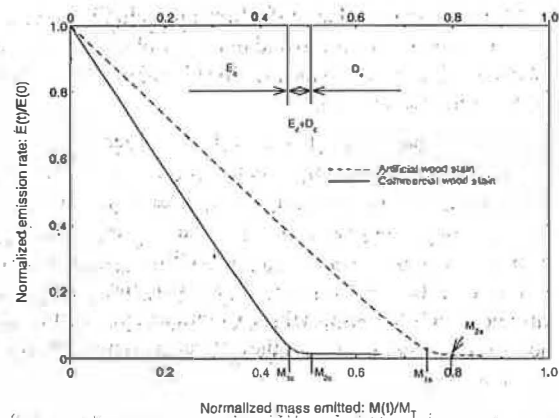


Figure 5 Normalized emission rate vs. normalized mass emitted. E_c , $E_c + D_c$ and D_c represent evaporative-controlled, transition, and diffusion-controlled periods for commercial wood stain, respectively.

Figure 5 gives the mean values of M_1 and M_2 for a curve showing the normalized emission rate vs. the amount emitted since time zero. Both figures indicate that the t_1 and t_2 (or M_1 and M_2) may be used to divide the emission process into three distinct periods, although their definitions are somewhat subjective: (1) an initial emission period from 0 to t_1 within which the VOC emission process is controlled by evaporation, (2) a transition period from t_1 to t_2 within which the emission is controlled by both the evaporation and internal diffusion, and (3) a period beyond t_2 (i.e., $t > t_2$) within which the emission process is controlled by internal diffusion (i.e., the portion of emissions controlled by evaporation becomes insignificant).

The values of t_1 and t_2 for the commercial wood stain were smaller than those of the artificial wood stain (Tables 3 and 4).

One of the reasons may be the presence of pigments/solids in the commercial wood stain, which would affect the VOC emission in two ways: (1) they contain some VOCs and these VOCs would have to diffuse to the surface before emitting into the air, resulting a reduced amount of VOCs emitted during the initial evaporation-controlled period and, hence, a smaller t_1 ; (2) the pigments would also be a barrier for the VOCs under them to diffuse to the surface, resulting in a decrease in the emission rate during the diffusion-controlled period.

Another reason may be the blend of other VOCs (in addition to the five VOCs in the artificial wood stain tested) in the commercial wood stain. Blending of the additional VOCs might have increased the volatility of the solvent mixture and led to a shorter t_1 . Industries often use different "blending" strategies to control the volatility of the solvent mixture and, hence, the drying rate of architectural coatings such as wood stains and paints. The blending effect would mainly affect the first emission period, which is an evaporation-controlled process. However, it does not explain the larger percentage of VOC mass that remained after the first emission period of the commercial wood stain compared to the artificial wood stain, which is most likely due to the presence of pigments/solids in the commercial wood stain.

As a result, t_1 and t_2 were shorter for the commercial wood stain (t_{1c} and t_{2c}) than the artificial wood stain (t_{1a} and t_{2a}), as shown in Figure 4. In addition, Figure 4 indicates that $t_{2a} - t_{1a} > t_{2c} - t_{1c}$, suggesting that the transition period for the commercial wood stain was shorter than for the artificial wood stain. These results collectively suggest that the effect of pigments and VOC blending on the VOC emission rates needs to be accounted for in future mathematical modeling of the emission process.

As shown in Figure 5, the VOC mass emitted during the evaporation-controlled period was 74.79% and 35.59% of the total emittable VOC content for artificial and commercial wood stains, respectively. This means that a significant amount of VOC mass was emitted in a relatively short period of time due to evaporation (on average, 5.64 and 3.09 hours for the artificial and commercial wood stains, respectively, as shown in Figure 4). The VOC mass emitted during the transition period represents only a small percent of the total emittable mass (4.99% and 3.01% for the artificial and commercial wood stains, respectively). The remaining VOCs emitted slowly during the internal diffusion-controlled period.

It should be noted that t_1 and t_2 are strongly dependent on the evaporative mass transfer rate, which, in turn, strongly depends on the environmental conditions such as the air velocity over the surface according to fundamental mass transfer theory (e.g., Kays and Crawford 1980). On the contrary, M_1 and M_2 may be less dependent on environmental conditions since they represent the amount of VOCs available for emission during the evaporation-controlled and the evaporation-controlled-plus-transition periods, respectively, regardless of the length of each period.

Repeatability of Emission Testing

Experimental measurements of VOC emission rates inevitably involve certain uncertainties that cause variations in emission testing results. The nine repeat tests (Table 4) can be used to evaluate the repeatability that can be practically achieved under a well-controlled environmental testing condition. Such information is needed for setting quality assurance criteria in a standard material emission testing method. It is also needed for validating mathematical models for predicting VOC emission rates.

The repeatability of the tests conducted can be assessed by the relative standard deviations (i.e., standard deviations divided by the mean values) of the characteristic parameters, which are listed in Table 4. In the assessment of the impact of material emissions on the indoor VOC concentrations, it is often necessary to know the emission rate as a function of time. Figure 6 shows how the relative standard deviation of the emission rate changes with time based on the results of the nine repetitive tests. It shows that the relative standard deviation of the emission rate was approximately 23% at time zero (conventionally called the initial emission rate). It dropped to a minimum value of about 12% at $t = 1$ hour, increased to the maximum value of about 30% at $t = 3$ hours, and then decreased (with a small fluctuation) with time to 25% at $t = 24$ hours. In general, it may be concluded that 25% to 30% relative standard deviation could be expected in the determination of the emission rate with the test procedure used in this study. This amount of uncertainty represents the case when the wood stain is applied onto an oak substrate as typically used to treat the floor of houses. Using a board with less grain variation (such as a maple wood board) as the substrate, less variation in the measured emission rate may be expected.

Using the proposed method for preparing test specimens, the amount of mass applied varied from 3.74 g to 4.39 g with a standard deviation of 9.8% for the artificial wood stain (Table 3) and varied from 3.67 g to 4.85 g with a standard deviation of 8.69% for the commercial wood stain (Table 4). These

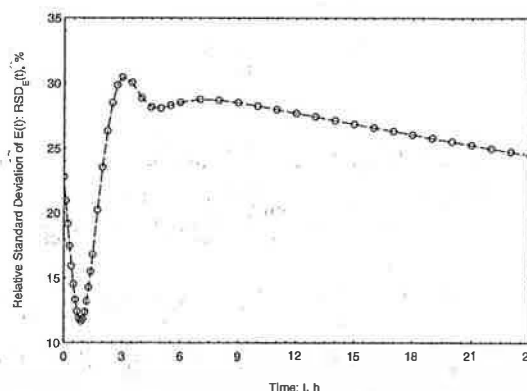


Figure 6 Variation of the relative standard deviation of emission rate with time.

results suggest that the amount of mass applied may be controlled within $\pm 10\%$ of a target amount using the application procedure proposed in this study. Based on the results of the artificial wood stain tests (A1a and A1b, A2a and A2b in Figure 2), it appears that the amounts of mass applied have little effect on the normalized weight vs. time curve if the amounts of mass applied can be controlled within 10% of each other. However, it is not clear whether a larger than 10% difference in the amount of mass applied will cause significant variations in the test results. Therefore, as a quality assurance criterion in a standard test procedure for "wet" coating materials, it is recommended that a criterion be set for the difference between the actual and target amount of wood stain applied.

Emission Rates Calculated from the Concentrations of the Return/Exhaust Air

Figure 7 shows the TVOC concentrations measured at the exhaust air for the nine tests conducted for the commercial wood stain. The amount of TVOC mass exhausted from the chamber can be calculated by the following equation:

$$M_e(t_n) = 0.5Q \sum_{i=0}^n [C_e(t_i) + C_e(t_{i+1})](t_{i+1} - t_i) \quad (12)$$

where

$M_e(t_n)$ = TVOC mass exhausted from time zero to time t_n , g;

Q = supply airflow rate, m^3/s ;

C_e = TVOC concentration of the exhaust air, g/m^3 ;

t = time, s;

i, n = indices representing sampling time points.

The emission rates can then be calculated by the following equation:

$$E(t_i) = (\Delta C_e / \Delta t)_{ti} + Q C(t_i) \quad (13)$$

where

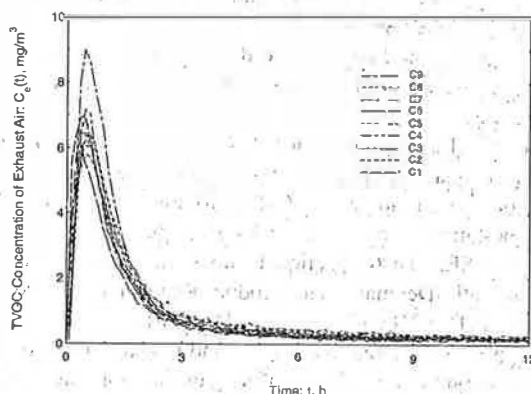


Figure 7 Measured TVOC concentrations at the chamber exhaust.

$$(\Delta C_e / \Delta t)_{ti} = 0.5 \{ [C(t_i) - C(t_{i-1})] / (t_i - t_{i-1}) + [C(t_{i+1}) - C(t_i)] / (t_{i+1} - t_i) \}$$

Figure 8 shows the TVOC mass exhausted from the air calculated from Equation 12. The results show that the TVOC mass exhausted during approximately the first one-and-a-half hour was significantly less than that measured by the electronic balance. This was probably caused by the time delay required for the VOCs to build up in the chamber and reach the chamber exhaust. However, the overall difference between the TVOC mass exhausted from the chamber and the weight loss measured by the electronic balance is considered to be within the experimental variation.

Figure 9 shows the emission rates calculated by Equation 13 (referred to as the chamber method) and the result measured directly by the electronic balance. The two methods agreed well with each other in general, confirming the validity

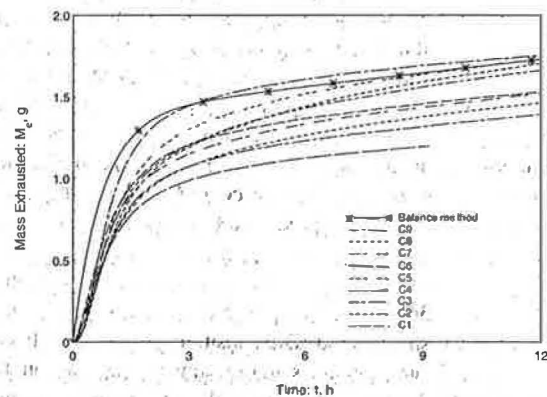


Figure 8 Mass exhausted from the chamber. The curve for the electronic balance method is obtained using the mean coefficients in Table 4.

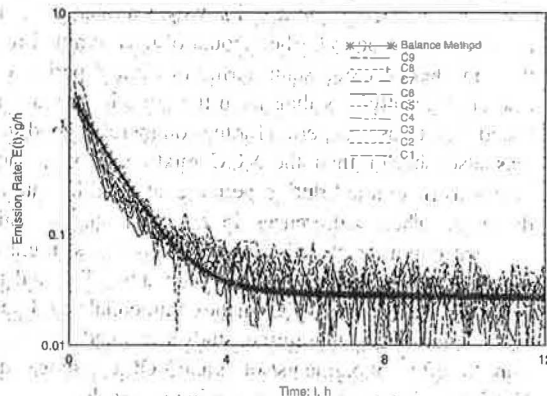


Figure 9 Emission rates of commercial wood stains as determined by the chamber method. The curve for the electronic balance method is obtained using the mean coefficients in Table 4.

of the "perfect mixing" assumption that is widely used in environmental chamber testing. The fluctuation of emission rates measured by the chamber method may be attributed to the experimental uncertainty in measuring the concentration as well as possible concentration fluctuations at the chamber exhaust of concentration as shown in Figure 9.

SUMMARY AND CONCLUSIONS

A method of testing VOC emissions using an electronic balance has been introduced in this study. A detailed procedure for preparing the test specimens of wood stains has also been developed. The method and procedure were used to determine the emission characteristics of an artificial and commercial wood stain when they were applied to an oak board. The following conclusions can be made from this study:

1. VOC emissions from the wood stains include both surface-evaporation and internal-diffusion processes. The entire emission time may be divided into three periods: (1) an initial period in which the emission rate was controlled by evaporation and characterized by a high and fast decaying emission rate, (2) a second (transition) period in which the emission transitioned from an evaporation-controlled to an internal diffusion-controlled process, and (3) a third period in which the emission rate was controlled by internal diffusion and was characterized by a low and slowly decaying emission rate. For the commercial wood stain tested, the length of the initial period was approximately three hours, and about 36% of the emittable VOC mass was emitted during this short period. The transition period was between 3 and 6.5 hours from the start of testing and only accounted for about 3% of VOC mass emitted. The remaining amount, about 61% of VOC mass, was emitted in the diffusion-controlled period.
2. Compared to the artificial wood stain (i.e., a VOC mixture containing major compounds identified from the commercial wood stain), the commercial wood stain had a shorter initial emission period. The amount of mass emitted from the commercial wood stain during this initial period was also significantly less than from the artificial wood stain tested. The transition period for the commercial wood stain was also shorter than the VOC mixture, leaving more VOCs to be emitted during period controlled by internal diffusion. These differences in emission characteristics between commercial and artificial wood stains might be attributed to the presence of the pigments/solids and the blending of additional VOCs in the commercial wood stain. The results suggest that further studies are needed to determine the effect of pigments/solids and VOC blending on the VOC emission rates of "wet" coating materials.
3. Emission rates determined using the electronic balance test method in this study may be expected to have a relative standard deviation of about 25% to 30% based on the results of nine repetitive tests conducted.

4. Using the concentrations measured at the full-scale chamber exhaust to determine the emission rate obtained results similar to those measured directly by the electronic balance method. This confirms the validity of the "perfect mixing" assumption that is widely used in environmental chamber testing.

The above results are useful for developing a standard VOC emission test method for "wet" coating materials in general. They are also useful for developing better mathematical models for predicting the VOC emission rates of "wet" coating materials.

ACKNOWLEDGMENT

The authors would like to thank the assistance of Dr. Malgosia Kanabus-Kaminska, Mr. Bob Magee, and Ms. Ewa Luszyk in conducting the experiments. The financial support from the members of Consortium for Material Emissions and IAQ Modeling (CMEIAQ), the Canadian Panel for Energy Research and Development (PERD), and National Research Council of Canada (NRCC) is appreciated.

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APPENDIX A

DETAILED PROCEDURES FOR PREPARING THE TEST SPECIMEN*

A1. Preparation of the Substrate

- A1.1 Randomly select a piece of oak board and plane the surface to produce a 10-mm-thick board.

* Note: The above procedure was adopted after experimenting with several alternatives (such as application with laboratory tissues, application directly with a wider brush, etc.) and was found to provide reasonably good control on the amount of wood stain applied while achieving good uniformity. The entire procedure took about 2.0 ± 1.0 minutes.

- A1.2 Cut the board into 250×240 pieces and sand them with grade 100 sandpaper.
- A1.3 Condition the substrate in a space maintained under the test conditions (i.e., 23°C and 50% RH) until their weight becomes constant (which takes a minimum of 72 hours).
- A1.4 Cover the bottom face and the four edges of each oak board with aluminum foil to minimize the adsorption of VOCs or moisture onto these surfaces.
- A1.5 Weigh the substrate (i.e., oak board with the aluminum foil) using an electronic balance.

A2. Application of Wood Stain

- A2.1 Place the conditioned oak substrate in a laboratory exhaust hood.
- A2.2 Gently stir the wood stain in its original container using a glass tube to ensure that the pigments and solvent are well mixed.
- A2.3 Pour approximately 10 mL wood stain into a 48-mm-diameter, 16-mm-high petri dish and soak a 15-mm-wide paint brush by dipping it fully into the wood stain in the petri dish.
- A2.4 Use a suction tube to spread 4 mL of wood stain onto the surface of the substrate, and immediately use the pre-soaked brush to uniformly distribute the wood stain on the substrate.
- A2.5 Place the prepared specimen on the electronic balance in the chamber for testing.