

KINETICS FOR DESICCATOR, JAR AND ALIKE TESTS FOR FORMALDEHYDE RELEASE FROM PARTICLEBOARD

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ABSTRACT

A kinetic equation linking test results with test parameters was derived for testing particleboard for formaldehyde release by means of a desiccator, jar, WKI, and similar tests based on undisturbed diffusion of formaldehyde from the board surface through the air into water. The equation was assessed by means of some experimental observations such as the independence of results on the number of test specimens and the asymptotic convergence of results obtained by different methods at increased temperature.

Keywords: Formaldehyde release, particleboard, test, kinetics.

INTRODUCTION

Formaldehyde release from pressed wood boards based on amino resins, such as particleboard and interior grade plywood, has become a subject of intensive investigation. A part of this effort is testing boards for formaldehyde emission. Numerous techniques have been developed (CCPA, Formaldehyde Council 1982; JSA 1977; NPA et al. 1982; Rybicky et al. 1983; CCAC and CCPA 1982; Roffael 1975; Sundin 1982; Myers and Nagaoka 1980, 1981; Christensen 1972; Roffael and Mehlhorn 1977; Berge and Mellegaard 1977; Meyer et al. 1983). Many of them are based on undisturbed diffusion of the emitted formaldehyde through the air and into still water (CCPA, Formaldehyde Council 1982; JSA 1977; NPA et al. 1982; Rybicky et al. 1983; Roffael 1975; Sundin, 1982). The experimental arrangement is such that the test specimens and a dish with water are kept in a tightly closed small container. After a specified time, the water is analyzed for the formaldehyde content and the latter (termed a desiccator or jar value, or similarly) serves as a measure for judging the board's capacity to emit formaldehyde. The U.S. (NPA et al. 1982) and Canadian (CCPA, Formaldehyde Council 1982) two-hour desiccator tests, the WKI or Roffael method (Roffael 1975) and its modified versions (Sundin 1982), the jar test (Rybicky et al. 1983) and some internally used, unpublished methods (CCAC and CCPA 1982) all fall into this category of tests.

For theoretical as well as practical reasons, knowledge of kinetic equations that govern the test mechanism is beneficial to the investigators. In this work, the test is subjected to kinetic considerations and analysis by means of differential rate equations for formaldehyde release and sorption. A kinetic relationship is obtained for the concentration of formaldehyde in the collecting water as a function of time and all the experimental parameters.

DERIVATION OF EQUATIONS

The following symbols are used in the text:

δ	partial differential.
d	total differential.
F_A, F_w	quantities of formaldehyde in air and water, respectively; (g).
$[F_A], [F_s], [F_w]$	concentrations of formaldehyde in air, board surface and water, respectively; (g cm ⁻³).
k_A, k_w	proportionality constants for the formaldehyde emission from board and the formaldehyde sorption by water, respectively; (dimensionless).
K_A, K_w	composite constants defined by Equations 7b and 7c, respectively.
m	equilibrium constant for formaldehyde sorption by water, defined as $[F_w]/[F_A]$ at equilibrium; (dimensionless).
n	equilibrium constant for formaldehyde emission from board, defined as $[F_A]/[F_s]$ at equilibrium; (dimensionless).
S_B, S_w	surface areas of board and water, respectively; (cm ²).
t	time of test; (s).
T_A	mass transfer of formaldehyde through air from board surface to water surface; (cm s ⁻¹).
T_w	mass transfer of formaldehyde through water from water surface to water bottom; (cm s ⁻¹).
V_A, V_w	volumes of air and water, respectively; (cm ³).

The kinetic treatment is based on the concept that the buildup of formaldehyde in the air inside the desiccator or jar is governed by (a) the formaldehyde release from the sample, and (b) the formaldehyde sorption by the water. These two processes can be mathematically described in the form of differential rate equations. Thus, for the emission,

$$\frac{\partial F_A}{\partial t} = k_A S_B T_A ([F_A]_{eq} - [F_A]) = k_A S_B T_A (n[F_s] - [F_A]) \quad (1a)$$

and for the sorption

$$-\frac{\partial F_A}{\partial t} = \frac{dF_w}{dt} = k_w S_w T_w ([F_w]_{eq} - [F_w]) = k_w S_w T_w (m[F_A] - [F_w]) \quad (1b)$$

The buildup of formaldehyde in the air is a sum of partial differentials for F_A , i.e.

$$\frac{dF_A}{dt} = \sum_{i=1}^i \left(\frac{\partial F_A}{\partial t} \right)_i = k_A S_B T_A (n[F_s] - [F_A]) - k_w S_w T_w (m[F_A] - [F_w]) \quad (2)$$

After dividing Eq. 2 by V_A so that dF_A becomes $d[F_A]$, and rearrangement,

$$\frac{d[F_A]}{dt} = \frac{k_A S_B T_A n [F_s]}{V_A} - [F_A] \left(\frac{k_A S_B T_A}{V_A} + \frac{m k_w S_w T_w}{V_A} \right) + [F_w] \frac{k_w S_w T_w}{V_A} \quad (3)$$

The forthcoming kinetic scheme can be solved when the steady-state approximation is applied to the concentration of formaldehyde in air. It may be appropriate to emphasize the principle of the steady-state approximation before proceeding further. The principle does not imply a constant concentration of the

TABLE 1. *Effect of number of test specimens on desiccator value.*

Laboratory	Number of test specimens	D.V. (mg/L)
Reichhold Ltd.	4	0.20
	8	0.14
Reichhold Ltd.	2	0.12
	8	0.06
Borden (Navratil 1982)	3	1.42
	7	1.38
Borden (Navratil 1982)	3	1.61
	7	1.98
Domtar (Kerekes 1982)	2	2.8
	4	2.2
	8	2.2

intermediate, as is often mistakenly assumed. Rather, it specifies that the change of the intermediate's concentration is numerically negligible in comparison with the sum of the other terms in the kinetic rate equation. The point becomes quite obvious (but rarely is presented this way in textbooks) when the differential term on the left-hand side (LHS) is transferred to the other terms on the right-hand side (RHS) of the equation. Thus, for Eq. 3,

$$\frac{d[F_A]}{dt} = \text{RHS} \quad (3a)$$

$$0 = \text{RHS} - \frac{d[F_A]}{dt} \quad (3b)$$

and after applying the steady-state approximation, i.e.

$$\text{RHS} \gg \frac{d[F_A]}{dt}$$

one obtains

$$0 = \text{RHS} \quad (4)$$

Equation 4 yields

$$[F_A] = \frac{(k_A S_B T_A n [F_S] / V_A) + ([F_W] k_W S_W T_W / V_A)}{(k_A S_B T_A / V_A) + (m k_W S_W T_W / V_A)} \quad (5)$$

Again, it may be appropriate to discuss the kinetic conditions under which the steady-state approximation is justified. These are (1) a fast (relative to the total time of experiment) initial buildup of the intermediate, or (2) a slow increase of intermediate concentration. The first case allows a high concentration of the intermediate when established at the early stages of the experiment's duration. Afterwards, its concentration is determined by an equilibrium constant of the process that generated the intermediate. In the case of a 2-hr desiccator or jar test, it would mean that the formaldehyde concentration in the air stabilizes very soon, e.g., in 10 min and remains almost (but not necessarily completely) constant during the remaining time of test.

The fast rate of formaldehyde buildup should not be confused with the equilibrium concentration being high; one does not imply the other. Should this case of the steady-state concentration system be found applicable to particleboard and plywood, it would not be limited to high-formaldehyde-release boards only, but rather have a general validity applicable to low emitters as well.

Continuing in the derivation of the final kinetic equation, $[F_A]$ (as given by Eq. 5) is substituted in Eq. 1b, and the new equation is divided by V_w so that dF_w be converted to $d[F_w]$. After rearrangement, the following relationship is obtained:

$$\frac{d[F_w]}{dt} = \frac{mnK_A K_w [F_s]}{K_A + mK_w V_w / V_A} + [F_w] \left(\frac{mK_w^2 V_w / V_A}{K_A + mK_w V_w / V_A} - K_w \right) \quad (6)$$

Equation 6 can be integrated and for the initial conditions that $F_w = 0$ when $t = 0$, it yields

$$[F_w] = mn[F_s] \left(1 - \exp \left(- \frac{K_A K_w V_A}{K_A V_A + mK_w V_w} t \right) \right) \quad (7)$$

$$\text{or} \quad [F_w] = mn[F_s] \left(1 - \exp \left(- \frac{k_A S_B T_A k_w S_w T_w}{k_A S_B T_A V_w + m k_w S_w T_w V_w} t \right) \right) \quad (7a)$$

$$\text{where} \quad K_A = k_A S_B T_A / V_A \quad (7b)$$

$$\text{and} \quad K_w = k_w S_w T_w / V_w \quad (7c)$$

Equation 7 describes the formaldehyde concentration in the water as a function of time of experiment and the experimental parameters. Its kinetic analysis provides some interesting answers, which are discussed in the next section.

ASSESSMENT OF THE KINETICS

It has been observed that when the number of test specimens in a desiccator or similar test is changed, the same result is obtained as before. Thus, when the Canadian 2-hr desiccator test (see Appendix for the method description) was employed for testing particleboard, the results presented in Table 1 were obtained by three different laboratories.

Additionally, at Fahrni Engineering AG, no difference for six and twelve test specimens was found in their internally developed jar-like test (CCAC and CCPA 1982).

The independence of the formaldehyde concentration in the water on the number of test specimens can be explained by means of Eq. 7, which predicts this observation to happen whenever product $K_A V_A$ is much larger than product $mK_w V_w$. Thus when

$$K_A V_A \gg mK_w V_w \quad (8a)$$

Equation 7 simplifies into Eq. 8b.

$$[F_w] = mn[F_s](1 - \exp(-K_w t)) \quad (8b)$$

Analysis of Eq. 8b reveals that a desiccator value or a jar value can become independent of S_B —the total surface of test specimens—and thus the number of test specimens. However, it still remains dependent on the water geometry, formaldehyde diffusion through the water, time, and the board tendency to release

TABLE 2. *Effect of temperature on desiccator and jar values.*

Temp (°C)	D.V. (mg/L)	J.V. (mg/L)	D.V./J.V.
5.0	0.82	0.20	4.10
15.0	1.24	0.56	2.21
25.5	2.06	1.30	1.58
35.0	3.68	2.80	1.31
45.0	9.60	8.60	1.12

formaldehyde. Considering the composition of K_w (Eq. 7c), the importance of T_w , which reflects the transfer of formaldehyde from the water surface into the bulk of the water, should be obvious. In practice, this means that a positive error in the test result can occur whenever the water is disturbed by vibration (when equipment is running on the same bench) or by movement (when the test container is carried or accidentally brushed against). All these undesirable interferences would increase the transport of formaldehyde through the water away from the water surface and thus the sorption of formaldehyde would be erroneously increased.

Recently, it was suggested (Rybicky et al. 1983) that at sufficiently high temperatures, all the desiccator and jar tests and other tests based on the same principle (water and samples being enclosed in a small container) would yield the same value. Two methods were employed, the Canadian 2-hr desiccator test and a jar test (see Appendix for the methods description). The geometries of the water samples and containers were different for the two tests. When the desiccator values and jar values were determined for different temperatures, the results presented in Table 2 were found.

So, with increasing temperature, ratio D.V./J.V. asymptotically approaches the unity. Again, this observation is consistent with Eq. 7. With increasing temperature, T_w assumes higher values because of increased diffusion in the water, and K_w increases further. For the ratio of $[F_w]$ values obtained by two different tests, the following relationship is true:

$$\frac{[F_w]_1}{[F_w]_2} = \frac{mn[F_s] (1 - \exp(-(K_w)_1 t))}{mn[F_s] (1 - \exp(-(K_w)_2 t))} \quad (9a)$$

Equation 9a simplifies into Eq. 9b.

$$\frac{[F_w]_1}{[F_w]_2} = \frac{1 - \exp(-(K_w)_1 t)}{1 - \exp(-(K_w)_2 t)} \quad (9b)$$

Examination of Eq. 9b reveals that as K_w values increase, the ratio of F_w values approaches the unity.

Equation 8B makes an interesting prediction: with a long enough time of experiment, all the tests under discussion should provide one identical result, namely $mn[F_s]$, as long as the tested specimens are equivalent in terms of formaldehyde release. Quite probably, a 48-hr test would be long enough. Since constant m is universal for a given temperature, the result would be a direct measure of the formaldehyde release from particleboard independent of test design.

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APPENDIX

Two methods were used in this work to assess the kinetics:

- 1) The Canadian Tentative Test Method for Emission of Formaldehyde from Wood Products, "Two-Hour Desiccator Test," was used, April 1, 1982 (CCPA, Formaldehyde Council 1982). In principle, it is the same as the U.S. 2-hr desiccator method. (NPA et al. 1982). The method utilizes a common glass desiccator (25 cm I.D. and volume of 10.5 L) with a porcelain desiccator plate (23 cm diameter). In the center of the plate is placed an inverted 400-ml glass beaker on top of which rests a glass petri dish (bottom only, 8.8 cm I.D., 2.0 cm high). The dish contains 25 ml distilled water. Eight test specimens, 7.0 cm × 12.7 cm, are cut from a board in such a way that they all have newly cut edges not less than 2 cm away from the original edge. After airing them for 7 days at 23 C ± 2 C and 50% ± 10% R.H. (unless specified otherwise), they are positioned vertically and equally spaced around the beaker. The desiccator is covered with a lid and kept at a temperature of 23 C ± 1 C for the duration of 120 min. Then the water in the petri dish is analyzed for the form-

aldehyde content by means of chromotropic acid, colorimetric method. The finding is referred to as a desiccator value.

- 2) A jar test (Rybicky et al. 1983) was employed and the results termed jar values. The analytical procedures remained the same as described for the Canadian 2-hr desiccator test. The collection of formaldehyde, however, was carried out in a small wide-mouth jar (Amber Ointment Jar, 500 ml) closed with a metal screw-cap that was lined with polyethylene. Four test specimens, 4.0 cm × 4.0 cm, cut from a board panel and preconditioned, if required, under the same rules as described in the desiccator method, were placed on edges on the bottom of the jar in the circular manner. A stainless steel wire screen (8-mm mesh) was placed on top of the specimens, and a glass petri dish (bottom only 4.0 cm I.D., 1.4 cm high) containing 10 ml distilled water was placed on the center of the screen. The jar was tightly closed and maintained at a required temperature, ± 0.5 C. After 120 min, the water was analyzed for formaldehyde by the chromotropic acid method.