

Nonequilibrium Partition Model for Predicting Flavor Retention in Microwave and Convection Heated Foods

Kris B. de Roos*[†] and Ernst Graf[‡]

Tastemaker B.V., Nijverheidsweg 60, 3771 ME Barneveld, The Netherlands, and
Tastemaker, 1199 Edison Drive, Cincinnati, Ohio 45216

A frequent problem associated with the application of flavor systems is the loss of flavor by volatilization during cooking or baking. This loss usually results in flavor profile distortion or even in a complete lack of flavor. Analysis of the factors that affect flavor volatilization has resulted in the development of a rigorous physicochemical model that relates flavor retention to the product-to-air partition coefficients of the flavor compounds and to the texture of the food. This so-called nonequilibrium partition model applies to both microwave and convection heating. Differences in flavor retention during microwave and convection heating can be explained on the basis of differences in temperature and moisture gradients in the product. Due to its general applicability, the model provides a useful tool for optimizing flavors for various bake applications.

Keywords: *Flavor volatilization; baking; microwave oven; convection oven; flavor partitioning; flavor-matrix interactions; computer modeling*

INTRODUCTION

The number of flavors suitable for bake applications is very limited. The reason is that the majority of flavors do not survive baking due to volatilization or chemical decomposition. Only a few examples exist of successful flavor applications in bakery products, such as the use of lemon flavor in cakes and vanillin in cookies.

The flavor of microwave (MW) heated food presents a special problem. Due to the absence of browning reactions that typically occur during baking in a conventional convection oven, MW products usually lack the desirable "baked" flavor. Therefore, flavors are often being used to increase palatability and consumer acceptance. Unfortunately, flavor retention during MW baking has turned out to be an even bigger problem than flavor retention during convection baking.

Several previous investigations studied flavor loss during MW heating of model systems (Shaath and Azzo, 1989; Steinke et al., 1989a,b; Stanford and McGorin, 1994; Lindstrom and Parliment, 1994; Graf and de Roos, 1994). The behavior of flavor compounds during MW heating has been described by two different theories, the delta T' theory and the vapor pressure theory.

According to the delta T' theory, the release of a flavor compound during MW heating can be predicted from its heat capacity and dielectric properties (Shaath and Azzo, 1989). Compounds with a high dielectric constant (high delta T' value) absorb more MW energy which is assumed to increase their chance of volatilization.

The vapor pressure theory, on the other hand, states that volatile compounds are lost from foods according to their vapor pressures in the respective media. In model systems of water and oil, a clear relationship was found to exist between volatility and flavor loss (Steinke et al., 1989a,b).

Recent publications have raised strong doubt concerning the validity of the delta T' theory. In fact, there

is convincing evidence that the delta T' theory fails to correctly predict flavor retention during MW heating (Stanford and McGorin, 1994; Lindstrom and Parliment, 1994; Graf and de Roos, 1994). At the same time, the evidence in favor of the vapor pressure theory increased (Stanford and McGorin, 1994; Lindstrom and Parliment, 1994). In a recent paper, a mathematical model was described that relates flavor loss during microwave heating with the vapor pressure of the individual flavor components in the food matrix (Graf and de Roos, 1994).

In general, much higher flavor losses are observed during MW heating than during convection heating (Steinke et al., 1989a,b; Stanford and McGorin, 1994). Steam distillation was assumed to be responsible for the increased flavor loss during MW heating, but currently no satisfactory model is available to provide a quantitative description of the difference in flavor retention during MW and convection heating.

The current paper presents a physicochemical mathematical model that explains the quantitative differences in flavor volatilization during MW and convection baking based on the vapor pressure theory. This so-called nonequilibrium partition model correlates flavor retention during heating with the product-to-air partition coefficients. The model lends itself to predict the behavior of a flavor composition during heat treatment and to optimize flavor composition for improved functionality in thermally processed products.

Factors Affecting the Rate of Volatilization. The partition coefficient and resistance to mass transfer are the major factors determining the rate and extent of flavor volatilization (de Roos and Wolswinkel, 1994). Most studies on volatilization of flavor compounds deal with partition phenomena, in particular with the effect of the chemical composition of the medium on the equilibrium vapor pressure (Buttery et al., 1971, 1973; Nelson and Hof, 1968; Williams and Rosser, 1981; Saravacos et al., 1990). These and other reports have shown that, of all common food ingredients, water, lipids, and ethanol have the strongest effect on the equilibrium headspace concentrations of the flavor chemicals (de Roos and Wolswinkel, 1994).

* Author to whom correspondence should be addressed.

[†] Tastemaker B.V., Barneveld.

[‡] Tastemaker, Cincinnati.

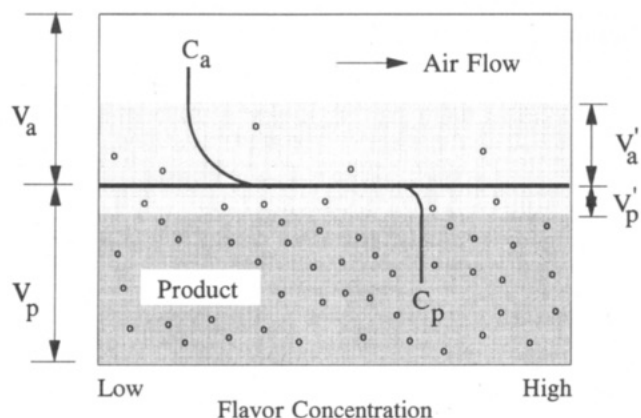


Figure 1. Partitioning of flavor compounds between product and air under nonequilibrium conditions. Partial equilibrium exists between the volume fractions V_a' and V_p' .

In contrast, the effect of mass transport has received only little attention. The few studies in this area show that increase of solution viscosity results in decrease of taste intensity. Some investigators attribute the suppression of flavor intensity to binding of the flavor compounds to the thickener (Godshall, 1988; Pangborn and Szczesniak, 1974; Godshall and Solms, 1992). Other investigators, however, ascribe the decreased intensity of flavor perception to inhibition of transport of flavor molecules from within the solution to the surface (Kokini et al., 1982; Baines and Morris, 1987; Cussler et al., 1979; Kokini, 1985; de Roos and Wolswinkel, 1994).

Among the first attempts to describe transfer of volatile compounds from liquid systems to air under nonequilibrium conditions is the "two-film" model (Whitman, 1923). More recently, the application of the "penetration theory" of mass transfer to the flavor release in the mouth was described (Overbosch et al., 1991). In our studies on flavor loss during microwave heating and flavor release in the mouth we used the nonequilibrium partition model to describe the transfer of volatile compounds from food to air (Graf and de Roos, 1994; de Roos and Wolswinkel, 1994). According to these theories, the potential *extent* of the flavor release is determined by the partition coefficient, whereas the *rate* at which equilibrium is achieved is determined by the resistance to mass transfer.

Nonequilibrium Partition Model. This model describes flavor release under nonequilibrium conditions as prevalent when phase equilibria are disturbed by continuous replacement of the headspace. A schematic diagram of the nonequilibrium partition model is shown in Figure 1. A full description of the model and the derivation of the equations has been given in a previous paper (de Roos and Wolswinkel, 1994). Therefore, we shall limit ourselves here to mentioning only the results.

The nonequilibrium partition model is premised on the following assumptions:

1. The flavor of the product is extracted consecutively with infinitesimal volumes V_a^* of air.
2. During each successive extraction, *complete* equilibrium is achieved only at the air-product interface in the small volume fractions V_p^* of product phase and V_a^* of air phase. These hypothetical volume fractions V_p^* and V_a^* are smaller but equivalent to the larger volume fractions V_p' and V_a' of Figure 1 in which only *partial* equilibrium exists.
3. After each extraction the initial flavor concentrations at the surface of the product are (partly) restored

by diffusion and turbulence before the next extraction takes place.

4. Differences in the diffusion coefficients between flavor components can be neglected. Since the diffusion constant does not vary much with flavor type, this simplification hardly affects the accuracy of the model.

The fraction of a flavor compound remaining in the food after n extractions with a volume V_a^* of air is then given by the equation

$$X_n/X_0 = \left[(V_p^*/V_p) [P_{pa}/(P_{pa} + V_a^*/V_p^*)] + (1 - V_p^*/V_p) \right]^n \quad (1a)$$

where X_0 is the initial quantity of flavor compound added to the system (g), X_n is the quantity of flavor compound present in the product after extraction with n hypothetical volumes V_a^* of air (g), V_a^* is the volume fraction of air that is in equilibrium with the volume fraction V_p^* of the product phase during each extraction step (L), V_p^* is the volume fraction of air that is in equilibrium with volume fraction V_a^* of air in the phase during each extraction step (L), V_p is the total volume of the solid/liquid product phase, excluding air inclusions (L), P_{pa} is the product-to-air partition coefficient, C_p/C_a , where C_p and C_a are the flavor compound concentrations in product and air phase, respectively (g/L), and n is the number of hypothetical extraction steps.

Or, if we substitute V_p^*/V_p by p_e (fraction of the product phase that is extracted during each extraction step):

$$X_n/X_0 = [p_e [P_{pa}/(P_{pa} + V_a^*/V_p^*)] + (1 - p_e)]^n \quad (1b)$$

In this equation, V_a^*/V_p^* is a measure for the resistance to mass transfer in the system. At high resistance to mass transfer in the product phase, the product volume fraction V_p^* that is in equilibrium with the air volume fraction V_a^* will be low, resulting in a high value of V_a^*/V_p^* . Differences in V_a^*/V_p^* reflect differences in product viscosity, product-air interfacial area, gas/steam flow rate, and turbulence in the product and gas phase. If the value of V_a^*/V_p^* exceeds the value of P_{pa} , then the release of the flavor compound is mainly mass transport controlled.

The use of eq 1 for predicting flavor release from partition data requires knowledge of the values of p_e , V_a^*/V_p^* , and n . In practice, this means that these "constants" have to be determined by least-squares fitting of experimental data for each food product. The experimental data are obtained by measuring the retention of a test sample of flavor compounds with known partition coefficients in the target application and calculating the unknown constants from the resulting set of equations. In fact, the equations contain only two unknowns, since n and p_e are interrelated. Therefore, we can substitute a very high value for n and then determine the values of p_e and V_a^*/V_p^* by least-squares analysis. Since differences in diffusion constants between flavor components can be neglected, the resulting equation holds for all other flavor compounds in this particular application.

MATERIALS AND METHODS

Materials. Flour, sugar, shortening, and vegetable oil were purchased at a local grocery store in Cincinnati. Flavor compounds were from Tastemaker stock in Barneveld, Holland. The flavor cocktail used in the bake experiments was dissolved in methanol. The solution contained 1% (w/v) of each

Table 1. Ingredient Composition of Cake Batter

ingredient	wt (g)		
	low fat	medium fat	high fat
flour	24.9	24.9	24.9
sugar	24.6	24.6	24.6
vegetable shortening	2.9	2.9	2.9
polysorbate	1.1	1.1	1.1
vegetable oil	0.0	14.4	22.4
flavor	0.1	0.1	0.1
water	46.4	32.0	24.0
total	100.0	100.0	100.0

flavor compound except for δ -2-decenolactone which was present at a concentration of 3% (w/v). The stock solution of internal standard for HPLC and GC analysis was prepared by adding 40 mg of veratrole (*m*-dimethoxybenzene) to 10 mL of methanol and was stored at 5 °C. All other chemicals and solvents were of analytical grade. Solvents used for extraction and preparative liquid chromatography were distilled prior to use.

Cake Preparation. (A) *Microwave Baking.* Ingredients listed in Table 1 were mixed by gentle stirring. Triplicate aliquots of 100 g were placed in glass dishes and baked in the microwave oven for 1, 2, and 3 min at full power (640 W) or for 2, 4, and 6 min at half power. Batter temperature was monitored continuously using a fluoroptic fiber probe (Luxtron instrument). Moisture loss was determined gravimetrically at the end of each time interval.

(B) *Convection Baking.* Samples were prepared as described above and baked in a convection oven for 40 min at 230 °C.

Flavor Isolation. (A) *From Batter.* Flavor extracts were prepared according to the modified "Folch" procedure (Chen et al., 1981). About 50 g of cake batter was weighed out accurately in a separatory funnel. An aqueous solution of 18% sodium chloride (120 mL) was added, followed by methanol (160 mL), dichloromethane (320 mL), and veratrole internal standard solution (50 μ L). The mixture was stirred vigorously for 30 min, and the resulting slurry was allowed to separate into an aqueous and an organic phase. If the organic phase was still turbid, the mixture was centrifuged to obtain clear phases. The resulting organic phase was separated and concentrated by distillation through a Vigreux column until the temperature started to rise. Dichloromethane (320 mL) was added, and distillation was continued to complete azeotropic removal of methanol. The concentrate (10 mL) was filtered through a 0.45 μ m Millex HV filter, and the concentrations of the flavor compounds in the extract were determined by reversed phase HPLC or GC (if GC was used, the sample was first cleaned up by gel permeation chromatography).

(B) *From Cake.* Sample preparation was the same as sample preparation of batter except for the addition of water to the cakes prior to extraction to compensate for the moisture loss during baking. The total weight of cake plus added water was about 50 g. The addition of water is necessary to assure that the partitioning (and thus the recovery) of the flavor compounds in the biphasic system is the same during each sample preparation.

Sample Cleanup by Gel Permeation Chromatography. The liquid chromatographic system consisted of a Spectra Physics Model SP 8700 XR pump, a Rheodyne 7125 injection valve with 1 mL loop, a Waters Model 403 differential refractometer, and a 250 \times 25 mm Lichrogel PS1 column (particle size, 10 μ m; exclusion limits, 100–2000 Da). The mobile phase was dichloromethane; flow rate, 3 mL/min. The injection volume was 1 mL, and solute concentration was <20% (to avoid peak distortion). The fraction containing the volatile compounds was collected and concentrated to 300 μ L by microdistillation prior to GC analysis.

Determination of Partition Coefficients. Air-to-oil partition coefficients were measured in olive oil at 25, 55, 80, and 100 °C according to the method of Etzweiler et al. (1980) using 30 \times 2 mm i.d. capillary tubes packed with XAD-4 resin (0.05–0.1 mm particle size). The solution was stirred to assure complete equilibration. A headspace of 1 L was collected from 10 mL of solution over a period of 3 h. After trapping, the

contents of the tubes were transferred quantitatively to minivials containing 200 μ L of dichloromethane. Concentrations in the liquid phase were determined by GC using internal standards. A blank consisting of flavor and resin in dichloromethane was run to adjust for adsorption to the resin.

Air-to-water partition coefficients were determined at 25, 90, and 95 °C by monitoring the decrease of the flavor compound concentrations in 15 mL of a stirred aqueous solution during stripping with nitrogen gas at a flow rate of 12.5 mL/min. To avoid evaporation of water from the solution, the nitrogen was presaturated with water vapor. Samples of 200 μ L were analyzed by HPLC after 15, 60, 120, and 240 min. The partition coefficients were calculated from the fraction of the flavor compound retained in the aqueous solution. Partition coefficients at 100 and 120 °C were calculated by extrapolation using the Clausius–Clapeyron equation (Table 2).

Determination of Delta T. Delta T was measured as described in the literature (Shaath and Azzo, 1989). A combination oven was used to allow measurement above the melting point of the flavor chemicals (70 °C). For that purpose, preweighed samples of the flavor chemical and water (35 g each) were thermostated in a water bath at 70 °C for at least 3 h and then placed on the turntable in the center of the oven which was thermostated at 70 °C (air temperature). The temperature of the samples was measured, and the samples were heated at full MW power (640 W) for 30 s. Then the temperatures were measured again. All measurements were done in duplicate. The delta T data are listed in Table 2.

High-Performance Liquid Chromatography (HPLC). Quantitative flavor analyses were performed by reversed phase HPLC on a 250 \times 4 mm Ultrasphere ODS column (Beckmann Instruments, Inc.) equipped with a 4 \times 4 mm Waters guard column. The compounds were eluted at 30 °C at a flow rate of 1 mL/min using the following nonlinear solvent gradient for elution: acetonitrile–water 20:80 (2.5 min); linear gradient to 75:25 in 22.5 min and then to 100% acetonitrile in 5 min. Finally, 100% acetonitrile for 10 min. The column was washed with dichloromethane for 15 min and then conditioned for the next analysis by washing with methanol (10 min) and acetonitrile–water 20:80 (20 min). Injection volume was 5 μ L or less to avoid peak distortion.

Gas Chromatography. Samples were run on a Carlo Erba HRGC Mega gas chromatograph equipped with splitter (split ratio: 1:100), FID detector, and a 60 m \times 0.25 mm glass capillary DB-1 column. Helium was used as the carrier gas. Column oven temperature: 50–280 °C at 2 °C/min and then maintained at 280 °C for 15 min.

Calculation of Flavor Retention. Flavor retention was calculated as

$$\% \text{ retained} = 100 \left(\frac{[A_i^c (W_s^c/A_s^c)] / (W^c + W^w)}{A_i^b (W_s^b/A_s^b) / W^b} \right)$$

where A_i and A_s are the peak areas of flavor compound i and internal standard s , respectively, W_s is the weight of internal standard s added to sample, W^b and W^c are the weights of batter and cake, respectively, and W^w is the weight of water lost during baking. Superscripts b and c refer to batter and cake, respectively.

RESULTS AND DISCUSSION

Cake was chosen as the food model for the present study. The reasons for this were its commercial significance as a widely sold MW food product and its uniform texture which is relatively independent of the fat content. The latter property allows the determination of the effect of the fat content on flavor partitioning with minimum interference from mass transport phenomena due to textural differences.

The flavor compounds were selected to cover a wide range of delta T values and water-to-air, oil-to-air, and

Table 2. Physical Properties of Flavor Compounds of Test Mixture

compd name	$\Delta T'$	$\log P_{wa}$			$\log P_{oa}$		
		25 °C	100 °C	120 °C	25 °C	100 °C	120 °C
2,3-dimethylpyrazine	0.9	3.86	2.27	1.95	4.00	2.85	2.62
raspberry ketone ^a	2.8	6.95	4.62	4.15	7.24	5.42	5.05
<i>p</i> -cresol	1.6	4.62	2.57	2.16	5.90	3.76	3.33
indole	1.5	4.92	2.54	2.06	6.53	4.35	3.91
δ -decenolactone	5.1	5.22	2.53	1.99	6.97	4.68	4.24
naphthalene	0.1	1.85	0.69	0.46	5.33	3.65	3.31
α -ionone	2.5	2.94	1.32	0.99	6.19	4.30	3.92

^a Systematic name: 4-(4'-hydroxyphenyl)butan-2-one.

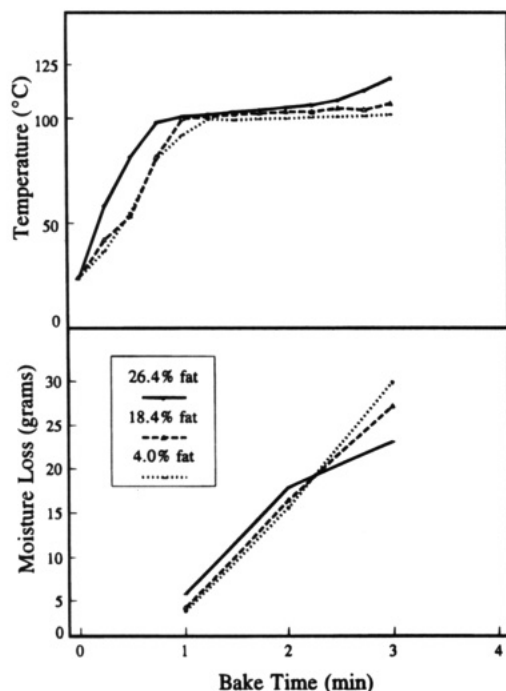


Figure 2. Effect of fat level on heating rate and moisture loss from cakes during MW baking.

oil-to-water partition coefficients (Table 2). In order to prevent complete flavor loss during baking, we chose chemicals exhibiting relatively low volatility. Other selection criteria were chemical stability and the HPLC separation and detection capabilities.

Since quantification of *p*-cresol and raspberry ketone by HPLC was often complicated by extraneous peaks generated during baking, the concentrations of these compounds were also determined by GC using flavor extracts cleaned up by gel permeation chromatography (only done for study of the validity of the $\Delta T'$ and the vapor pressure theory).

Flavor Volatilization during Microwave Heating. Volatilization during MW baking was first investigated under standard heating conditions, i.e., full MW power and 3 min bake time. Figure 2 depicts the effect of fat content on the heating rate and moisture loss. During the first 30–45 s, the MW energy is used almost exclusively to increase the batter temperature to about 100 °C. Then a period follows during which time the temperature remains constant due to the evaporation of water. When almost all water has evaporated, the temperature continues to rise again (most pronounced with the high fat (low moisture) cake). During the whole bake period, batters with highest fat content exhibit the highest temperature.

The retention of volatile compounds in the cake during baking at full microwave power (640 W) is shown in Figure 3. The graph clearly shows the relationship

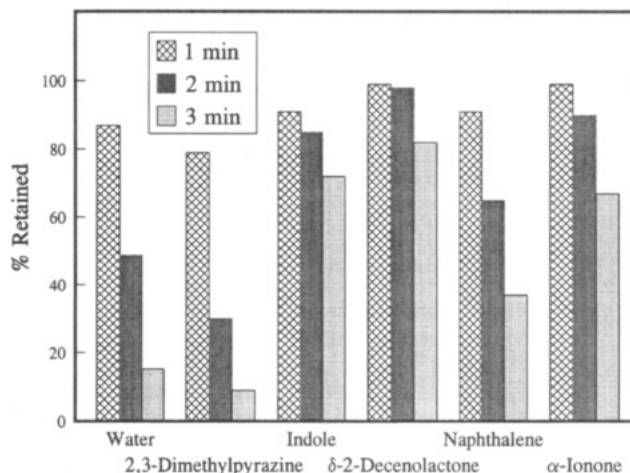


Figure 3. Retention of volatiles in cakes as a function of MW bake time.

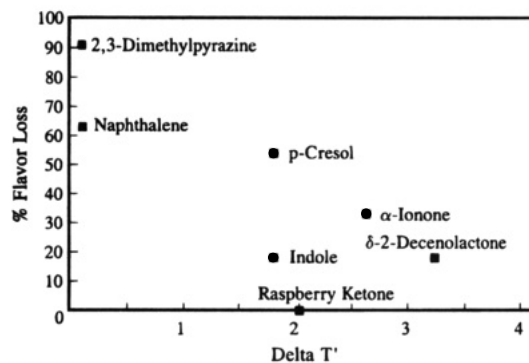


Figure 4. Relationship between $\Delta T'$ and flavor retention after MW baking for 3 min.

between flavor and moisture loss. Such a relationship is not surprising since effective aroma release requires not only high temperature but also formation of steam to facilitate mass transport from the product to the surrounding air.

The relationship between flavor volatilization and $\Delta T'$ is shown in Figure 4. The relationship found by us is in contradiction with the $\Delta T'$ theory: Compounds with a low $\Delta T'$ value (naphthalene and 2,3-dimethylpyrazine) show highest loss, whereas compounds with a high $\Delta T'$ value (raspberry ketone and δ -2-decenolactone) show lowest loss. This is just opposite to what is predicted. The obvious explanation for these results is that all of the $\Delta T'$ measurements were performed using pure compounds with no consideration being given to the flavor–food matrix interactions. In foods, however, the microwave energy absorbed by flavor molecules is dissipated as heat to the surrounding medium. Therefore, the results obtained with pure flavor compounds are irrelevant to their behavior in the food. Other investigators working with

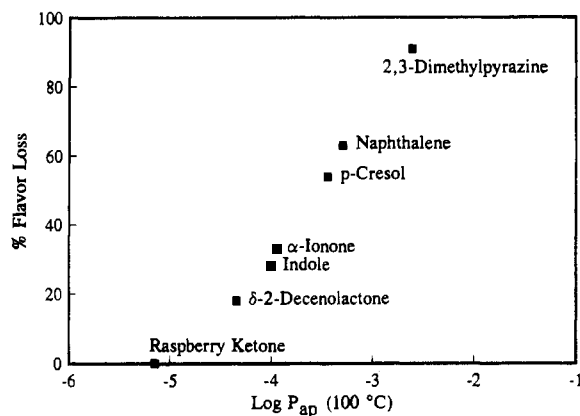


Figure 5. Relationship between $\log P_{ap}$ and flavor retention in cakes during MW baking for 3 min. $\log P_{ap}$ ($= -\log P_{pa}$) was calculated using eq 2 with f_w representing the average water content during the bake period.

food model systems arrived at the same conclusion (Lindstrom and Parliment, 1994; Stanford and McGorin, 1994).

A much better relationship was found to exist between flavor retention and the batter-to-air partition coefficients of the volatile components at 100 °C (see Figure 5). The batter-to-air partition coefficients were estimated by assuming that only the ratio of oil-to-water determines the partitioning of the flavor compounds between batter and air. In that case, the batter-to-air partition coefficients are given by

$$P_{pa} = C_p/C_a = (f_o C_o + f_w C_w)/C_a = f_o P_{oa} + f_w P_{wa} \quad (2)$$

where $f_o = V_o/(V_o + V_w)$, $f_w = V_w/(V_o + V_w)$, C_o is the concentration of the flavor compound in the oil/fat phase (g/L), C_w is the concentration of the flavor compound in the water phase (g/L), $P_{oa} = C_o/C_a$ is the oil-to-air partition coefficient, and $P_{wa} = C_w/C_a$ is the water-to-air partition coefficient.

For the relationship of Figure 5, we used product-to-air partition coefficients that correspond with the average water content of the batter during the whole MW bake period.

The results of the above experiments strongly suggest that flavor volatilization in the MW oven is controlled by the same physical laws as flavor volatilization during conventional heating. This result has prompted us to investigate the applicability of the nonequilibrium partition model to the prediction of flavor retention during MW and convection heating in more detail.

Prediction of Flavor Retention during MW Heating. In order to allow application of the nonequilibrium partition model to flavor retention in cakes, the following assumptions were made:

1. The ratio of water-to-oil determines the partitioning of volatiles between air and product. In general, the hydrophobicity of proteins and starch is too low to have a significant influence on the hydrophobic-hydrophilic balance in the food. This assumption only holds as long as some water or fat is present in the product. In low and no fat foods specific interactions between proteins and certain flavor molecules, such as phenols, may play a more prominent role.

2. Equilibrium exists in the biphasic oil-water system. Under these conditions, the relationship of eq 2 holds.

3. The flavor compounds are released at 100 °C, i.e., at the boiling point of water.

Table 3. Observed versus Predicted Retention (Percent) of Volatiles during Microwave Baking of Medium Fat Cakes

	1 min		2 min		3 min	
	obsd	calcd	obsd	calcd	obsd	calcd
water	83		49		15	
2,3-dimethylpyrazine	79	78	30	31	9	10
indole	91	97	85	87	72	73
δ-decenolactone	99	98	98	93	82	85
naphthalene	91	89	65	58	37	33
α-ionone	99	97	90	85	67	70
values of variables	first min		second min		third min	
$p_e (\times 10^{-6})$	8.75		10.6		13.0	
V_a^*/V_p^*	800		1000		2000	
n	41 650		122 600		108 000	
av water content (% w/w)	30.0		21.8		10.3	

4. The steam evolved serves as a carrier that transfers the volatile compounds across the product-air boundary. This implies that flavor losses are related to the amount of water that evaporates during baking.

5. The moisture content remains uniformly distributed throughout the product in spite of its decrease with bake time.

The flavor retention during microwave baking of the cakes can be approximated by the product Π of the fractions retained during the subsequent heating periods

$$F_{total} = \prod_{t=1}^{t=n} F^t \quad (3)$$

where Π is the product (mathematical), F_{total} is the fraction of flavor molecule retained during the whole bake period, and F^t is the fraction of flavor molecule retained during bake period t .

In our fitting experiments, the number of hypothetical extraction steps n was related to water loss as follows: $n = 10\,000 \times \text{mL of water evaporated}$. Furthermore, we distinguished three heating periods: first, second, and third minute. The fitting of calculated to observed flavor retention is then relatively easy (Table 3). Best fits were obtained for values of V_a^*/V_p^* ranging from 800 to 2000. V_a^*/V_p^* increases with bake time due to the parallel increase in batter viscosity which raises the resistance to mass transfer.

It is noteworthy that the value of $p_e (V_p^*/V_p)$ increases with bake time despite higher resistance to mass transfer in the cakes. The increase in specific surface area due to steam leavening and formation of a spongy texture may account for this apparent anomaly.

Effect of Fat Content on Microwave Flavor Retention. As shown in Figure 6, the product-to-air partition coefficients of all flavor compounds increase with the fat content of the batter. On basis of this relationship between fat and product-to-air partition coefficient, it may be anticipated that the retention of the flavor compounds during baking will increase with increasing fat content.

In general, the results of the bake experiments confirm the expected increase in flavor retention with fat content (Figure 7). An exception, however, is the behavior of 2,3-dimethylpyrazine. For this hydrophilic flavor compound, the higher temperature of the high fat cake apparently has a more pronounced effect on the rate of volatilization than the higher fat content. For most other flavor compounds, however, the decrease in

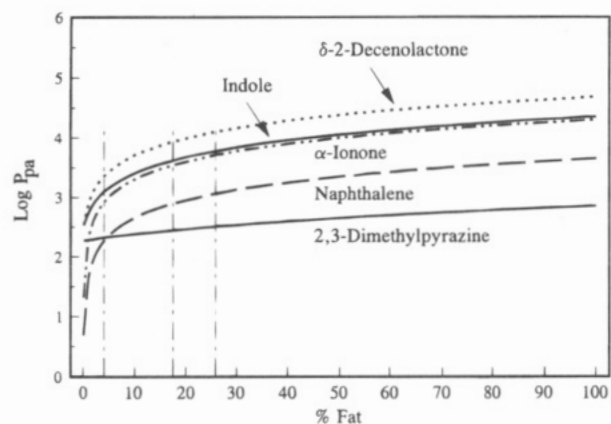


Figure 6. Product-to-air partition coefficients as a function of the fat content of the cake batter (calculated using eq 2).

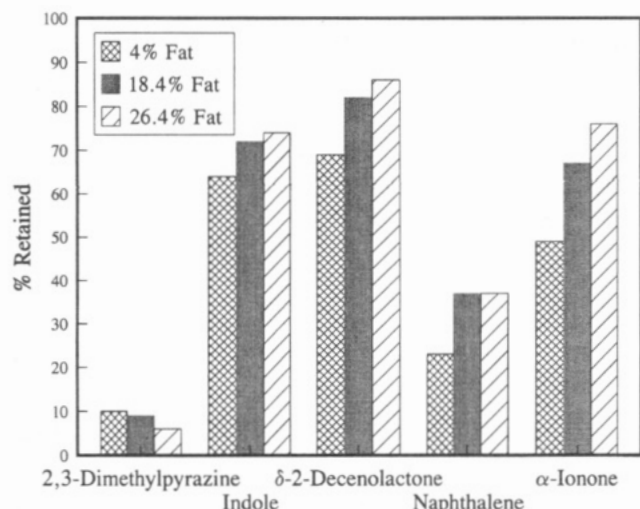


Figure 7. Effect of fat content on flavor retention in cakes during MW baking.

Table 4. Observed versus Predicted Retention (Percent) of Volatiles during Microwave Baking of Low Fat Cakes

	1 min		2 min		3 min	
	obsd	calcd	obsd	calcd	obsd	calcd
water	92		66		36	
2,3-dimethylpyrazine	77	70	30	31	10	14
indole	97	90	77	70	64	57
delta-decenolactone	89	94	78	81	69	73
naphthalene	68	73	36	37	22	21
alpha-ionone	86	88	65	65	49	51
values of variable	first min		second min		third min	
$p_e (\times 10^{-6})$	13.2		8.92		7.29	
V_a^*/V_p^*	585		800		875	
n	38 200		118 200		142 300	
av water content in (% w/w)	44.6		36.8		23.7	

volatility with fat content greatly outweighs the temperature effect.

Tables 4 and 5 compare observed and calculated flavor retention for high and low fat cakes. In general, a good fit is obtained. The values of V_a^*/V_p^* demonstrate that the increase in resistance to mass transfer with bake time is much more pronounced with high fat than with low fat cakes. The same holds true for the change of p_e with bake time. This can be explained by the relatively large change in composition and texture of the high fat cakes with bake time as compared to the low fat cakes.

Flavor Retention during Convection Heating.

Figure 8 compares the rates of moisture loss during MW

Table 5. Observed versus Predicted Retention (Percent) of Volatiles during Microwave Baking of High Fat Cakes

	1 min		2 min		3 min	
	obsd	calcd	obsd	calcd	obsd	calcd
water	76		26		4	
2,3-dimethylpyrazine	66	64	21	23	6	7
indole	95	96	87	87	75	78
delta-decenolactone	97	98	97	93	86	88
naphthalene	84	84	53	57	38	37
alpha-ionone	97	95	88	86	76	75
values of variables	first min		second min		third min	
$p_e (\times 10^{-6})$	12.1		13.1		31.0	
V_a^*/V_p^*	800		1000		1500	
n	58 100		120 800		51 900	
av water content (% w/w)	21.2		12.2		3.62	

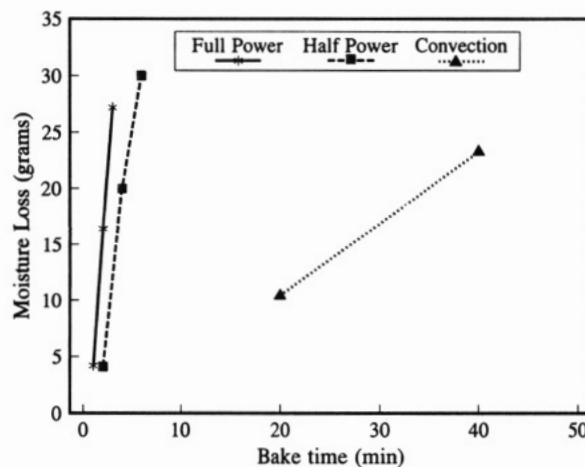


Figure 8. Effect of heating method on rate of moisture loss from medium fat cakes.

and convection heating. MW heating was done at two different power settings: full power (3 min) and half power (6 min). Remarkable is the comparatively low rate of moisture loss during convection baking. After 40 min at 230 °C in the convection oven, the moisture loss is still less than after 3 min at full power in the MW oven. In contrast, a lower rate of heating in the MW oven results in higher moisture loss (at same energy input). Apparently, the intermittent MW heating mode at half power allows for partial phase re-equilibration and vaporization during alternating idle intervals.

The different MW bake conditions affect flavor retention in about the same way as they do moisture retention (Figure 9). Flavor retention during convection heating, however, is different. Whereas the retention of the most volatile compounds is in line with moisture loss (i.e., higher than during MW heating at full power), the least volatile compounds (indole, delta-2-decenolactone, and alpha-ionone) show a considerably lower retention than anticipated on the basis of moisture loss. The most likely explanation for this observation is that the higher surface temperature of the cake in the convection oven results in a more exhaustive surface stripping of volatiles (retention of all flavor compounds in crust tends to be low).

One of the factors contributing to the relatively high retention of the more volatile compounds during convection heating is the almost negligible flavor loss from the core of the cake (retention of all flavor compounds is about 100%). The overall effect of the different temperature and moisture gradients in the cakes is that

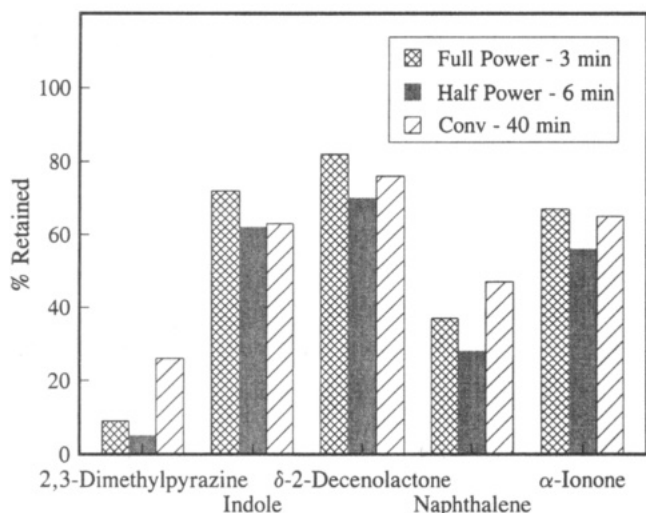


Figure 9. Effect of heating method on flavor retention in medium fat cakes.

flavor loss during convection heating is more uniform than during MW heating.

Prediction of Flavor Retention during Convection Heating. Due to the temperature and moisture gradients in the cakes during convection baking, modeling of flavor volatilization is much more complex than that during MW baking. In the convection oven, flavor and water start to evaporate from the outside resulting in the formation of an almost anhydrous crust. Water plus flavor evaporating from the interior parts of the cake have to pass this crust. The consequence is that flavor compounds with relatively low affinity to the fat phase will be stripped from the crust due to its higher temperature, whereas compounds with relatively high fat affinity (high value of P_{ow}) will be resorbed. Unfortunately, the mathematics of quantifying the effects of desorption and resorption of flavor molecules in the cake is very complex.

To allow application of the nonequilibrium partition model to the prediction of flavor retention during convection heating, we used a simplified model in which we consider separate and independent flavor loss from three different areas of the cake. According to this model, flavor retention in the cake is the average of flavor retention in the crust (c), the core (middle) of the cake (m), and the intermediate area between core and crust (i)

$$F_{total}^t = V_c^t F_c^t + V_i^t F_i^t + V_m^t F_m^t \quad (4)$$

where F_{total}^t is the fraction of a flavor compound retained in the whole cake after t minutes of heating, F_c^t , F_i^t , and F_m^t are the flavor fractions retained in the crust, intermediate part, and the core of the cake after t minutes of heating, and V_c^t , V_i^t , and V_m^t are the volume fractions of the crust, intermediate part, and the core of the cake after t minutes of heating. $V_c^t + V_i^t + V_m^t = 1$, and V_c^t increases with bake time, whereas V_m^t decreases.

For our calculations we assumed that the flavor loss from the three different areas of the cake during baking take place under the following conditions:

Middle of the Cake (m). Temperature is below 100 °C. Therefore, the rate of flavor volatilization from this part of the cake is negligible.

Intermediate Part between Crust and Core (i). In this part of the cake about the same conditions prevail as

Table 6. Observed versus Predicted Flavor Retention (Percent) after Conventional Baking of Medium Fat Cakes

compd name	calcd				obsd
	F_c^{40}	F_i^{40}	F_m^{40}	F_{total}^{40}	F_{total}^{40}
water					27
2,3-dimethylpyrazine	8.8	22.8	100.0	26	26
indole	47.2	88.6	100.0	65	63
δ-decenolactone	66.2	94.3	100.0	78	76
naphthalene	19.2	60.0	100.0	42	47
α-ionone	47.7	87.3	100.0	65	65
values of variables	crust	intermed	middle		
p_e ($\times 10^{-6}$)	8.68	10.4	0		
V_a^*/V_p^*	3000	800	0		
n	318 000	240 000	0		
water (% w/w)	0.20	8.0	32.0		
T (°C)	120	100	<100		
V^{40}	0.60	0.25	0.15		

during MW baking. Moisture content is intermediate and the temperature is 100 °C. It is from this part of the cake that the major part of the steam is generated.

Crust (c). In the crust the moisture content is almost zero and the temperature is higher than 100 °C. In our calculations we assumed that the $T = 120$ °C. Flavor losses from this part of the cake are relatively high, because steam that has evolved in the intermediate part of the cake strips additional amounts of volatile compounds from the crust.

Table 6 shows the observed versus calculated flavor retention during convection baking. In general, a good fit is obtained. This is in spite of the use of a simplified mathematic model of flavor volatilization during convection heating. A minor exception is naphthalene, for which the calculated retention is slightly lower than the observed retention. This might indicate that resorption of this very hydrophobic flavor compound by the crust cannot be completely neglected. Another possible explanation is that naphthalene interacts relatively strongly with starch and/or proteins (not taken into account).

The above results demonstrate that the nonequilibrium partition model applies to both MW and convection heating. The differences in flavor retention during MW and convection heating can be explained on the basis of the differences in the temperature and moisture gradients in the cakes. No microwave specific effects were observed. The ability to describe flavor loss during baking by a mathematical model implies that flavor retention can be predicted. This allows for optimization of flavor performance in baked products by (a) reformulating flavors to compensate for differential bake losses due to volatilization and (b) replacing the most volatile compounds with less volatile alternatives.

ACKNOWLEDGMENT

We thank C. Wolswinkel for conducting the chemical analyses and A. C. Stijnman for technical assistance with the bake experiments.

LITERATURE CITED

- Baines, Z. V.; Morris, E. R. Flavor/taste perception in thickened systems: The effect of guar gum above and below c^* . *Food Hydrocolloids* **1987**, *1*, 197–205.
- Buttery, R. G.; Bomben, J. L.; Guadagni, D. G.; Ling, L. C. Some considerations of the volatilities of organic flavor compounds in foods. *J. Agric. Food Chem.* **1971**, *19*, 1045–1048.

- Buttery, R. G.; Guadagni, D. G.; Ling, L. C. Flavor compounds: Volatilities in vegetable oil and oil-water mixtures. Estimation of odor thresholds. *J. Agric. Food Chem.* **1973**, *21*, 198-201.
- Chen, I. S.; Chen, C.-S. J.; Sheppard, A. J. Comparison of methylene chloride and chloroform for the extraction of fats from food products. *J. Am. Oil Chem. Soc.* **1981**, *58*, 599-601.
- Cussler, E. L.; Kokini, J. L.; Weinheimer, R. L.; Moskowitz, H. R. Food texture in the mouth. *Food Technol.* **1979**, *33*(10), 89-92.
- de Roos, K. B.; Wolswinkel, C. Non-equilibrium partition model for predicting flavor release in the mouth. In *Trends in Flavor Research*; Maarse, H., Van der Heij, D. G., Eds.; Elsevier Science: Amsterdam, 1994; pp 15-32.
- Etzweiler, F.; Neuner-Jehle, N.; Senn, E. Use of quantitative headspace analysis for investigation of behavior of odor compounds in soaps and detergents (German). *Seifen, Oele, Fette, Wachse* **1980**, *106*, 419-427.
- Godshall, M. A. The role of carbohydrates in flavor development. *Food Technol.* **1988**, *42*(11), 71-78.
- Godshall, M. A.; Solms, J. Flavor and sweetener interactions with starch. *Food Technol.* **1992**, *46*(6), 140-145.
- Graf, E.; de Roos, K. B. Nonequilibrium partition model for prediction of microwave flavor release. In *Thermally Generated Flavors. Maillard, Microwave and Extrusion Processes*; Parliment, T. H., Morello, M. J., McGorin R. J., Eds.; Symposium Series 543; American Chemical Society: ACS Washington, DC, 1994; pp 437-448.
- Kokini, J. L. Fluid and semi-solid food texture and texture taste interactions. *Food Technol.* **1985**, *39*(11), 86-94.
- Kokini, J. L.; Bistany, K.; Poole, M.; Stier, E. Use of mass transfer theory to predict viscosity-sweetness interactions of fructose and sucrose solutions containing tomato solids. *J. Texture Stud.* **1982**, *13*, 187-200.
- Lindstrom, T. R.; Parliment, T. H. Microwave volatilization of aroma compounds. In *Thermally Generated Flavors. Maillard, Microwave and Extrusion Processes*; Parliment, T. H., Morello, M. J., McGorin R. J., Eds.; Symposium Series 543; American Chemical Society: ACS Washington, DC, 1994; pp 405-413.
- Nelson, P. E.; Hof, J. E. Food volatiles: Gas chromatographic determination of partition coefficients in water-lipid systems. *J. Food Sci.* **1968**, *33*, 479-482.
- Overbosch, P.; Afterof, W. G. M.; Haring, P. G. M. Flavor release in the mouth. *Food Rev. Int.* **1991**, *7*, 137-184.
- Pangborn, R. M.; Szczesniak, A. S. Effect of hydrocolloids and viscosity on flavor and odor intensities of aromatic flavor compounds. *J. Texture Stud.* **1974**, *4*, 467-482.
- Saravacos, G. D.; Karathanos, V.; Marinou-Kouris, D. Volatility of fruit aroma compounds in sugar solutions. In *Flavors and Off-flavors*; Charalambous, G., Ed.; Elsevier: Amsterdam, 1990; pp 729-738.
- Shaath, N. A.; Azzo, N. R. Design of flavors for the microwave oven-The Delta T theory. In *Thermal Generation of Aromas*; Parliment, T. H., McGorin, R. J., Ho, C.-T., Eds.; ACS Symposium Series 409; American Chemical Society: Washington, DC, 1989; pp 512-518.
- Stanford, M. A.; McGorin, R. J. Flavor volatilization in microwave food model systems. In *Thermally Generated Flavors. Maillard, Microwave and Extrusion Processes*; Parliment, T. H., Morello, M. J., McGorin R. J., Eds.; ACS Symposium Series 543; American Chemical Society: Washington, DC, 1994; pp 414-436.
- Steinke, J. A.; Frick, C. M.; Gallagher, J. A.; Strassburger, K. J. Influence of microwave heating on flavor. In *Thermal Generation of Aromas*; Parliment, T. H., McGorin, R. J., Ho, C.-T., Eds.; ACS Symposium Series 409; American Chemical Society: Washington, DC, 1989; pp 512-518.
- Steinke, J. A.; Frick, C. M.; Gallagher, J. A.; Strassburger, K. J. Influence of microwave heating on flavor. In *Thermal Generation of Aromas*; Parliment, T. H., McGorin, R. J., Ho, C.-T., Eds.; ACS Symposium Series 409; American Chemical Society: Washington, DC, 1989b; pp 519-525.
- Whitman, W. G. The two-film theory of gas absorption. *Chem. Metall. Eng.* **1923**, *29*, 146-148.
- Williams, A. A.; Rosser, P. R. Aroma enhancing properties of ethanol. *Chem. Senses* **1981**, *6*, 149-153.

Received for review January 9, 1995. Accepted June 6, 1995.*

JF950019Z

* Abstract published in *Advance ACS Abstracts*, July 15, 1995.