*Food Engineering Progress*
*Vol. 14, No. 4. pp. 354~358 (2010.11)*

산업식품공학
Food Engineering Progress

**Research Note**

# Absorption of d-Limonene in Orange Juice into a Laminated Food Package Studied with a Solid Phase Micro-extraction Method

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**Abstract**

The methods for determining the diffusion parameters for the diffusion of d-limonene, a major volatile compound of orange juice, through a multi-layered food packaging material and predicting its absorption into the packaging material have been investigated. The packaging material used was the 1.5-mm thick multi-layered packaging material composed of high impact polystyrene (HIPS), polyvinylidene chloride (PVDC), and low density polyethylene (LDPE). Orange juice was placed in a cell where volatiles were absorbed in the sample package and kept at $23\pm2^{\circ}C$ for 72 hr. The d-limonene absorbed in a 1.5-mm thick multi-layered food packaging material was analyzed by a solid phase micro-extraction (SPME). The absorption parameters for the absorption of d-limonene in the packaging material were determined and absorption of d-limonene into the packaging material was predicted using absorption storage data. The SPME desorption at $60^{\circ}C$ for 1 hr resulted in the most sensitive and reproducible results. The diffusion coefficients of d-limonene in the packaging material and the partition coefficient at $23\pm2^{\circ}C$ were approximately $1\text{-}2\times10^{-12}$ $m^2/s$ and 0.03, respectively. The absorption profile no earlier than 30 hr was fit well by a model derived from the Fick's law.

**Key words:** flavor absorption, diffusion coefficient, d-limonene, multi-layered package, solid phase micro-extraction

## Introduction

Synthetic polymers are used as the most common packaging materials for juice products. The polymers form juice packages in either single-material structures or multi-layered-material (laminate) structures. The absorption of orange juice flavors by polymeric packaging materials may result in imbalances of flavor profiles, which makes the product less acceptable to consumers (Baner et al., 1991; Sajilata et al., 2007). Absorption depends highly on polarities and chemical structural similarities between flavor compounds and packaging materials or their functional groups (Landois-Garza & Hotchkiss, 1987). Hydrocarbon and ester compounds were absorbed into low density polyethylene (LDPE) at a much higher levels than aldehyde and alcohol compounds (Halek & Meyers, 1989).

Orange juice, which is the most popular juice, has been consumed 2,214,174 tons in the world in 2008 (USDA, 2009). A cyclic terpene, d-limonene, is responsible for about 95% of total flavor compounds of orange juice (Kutty et al., 1994; Mirhosseini et al., 2007). The loss of d-limonene in orange juice results in degradation of flavor (Mannheim & Passy, 1987; Pieper et al., 1992) and antioxidant properties of orange juice (Huang et al., 1994; Kim et al., 1995). Due to the importance of d-limonene, it has been used as a flavor indicator in the studies of orange juice quality.

Methods for analyzing flavor compounds absorbed in polymer materials have been developed. Dynamic headspace analysis, also known as purge-and trap analysis was applied to overcome the lack of sensitivity of static headspace analysis (Kujawinski et al., 2010). However, dynamic headspace analysis is an expensive, time-consuming, labor-intensive method and less reproducible than the static headspace analysis (Song et al, 1997). Solid phase micro-extraction (SPME) is inexpensive, rapid, reproducible and simple when it is compared to other well established techniques for the analysis of volatile compounds of food, such as solvent extraction, simultaneous distillation extraction, and purge-and trap analysis (Zhang & Pawliszyn, 1993; Krahn et al., 2010). SPME is significantly faster and easier than solvent extraction methods and does not require the use of toxic and expensive solvents (Ebeler et al., 2000). The objectives of the research were to develop a headspace SPME gas chromatography (SPME-GC) method for analysis of an orange juice flavor compound absorbed in a multi-layered polymeric packaging material and

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Received September 16, 2010; revised October 21, 2010; accepted October 23, 2010

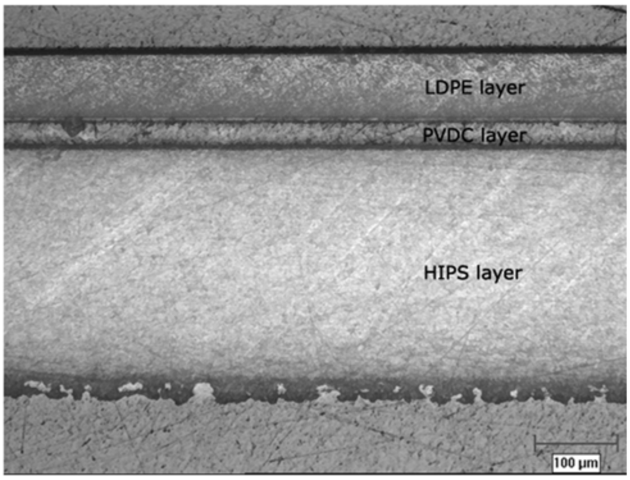

**Fig. 1. Cross-sectional image of the 1.5-mm-thick HIPS/PVDC/LDPE multi-layered film.**

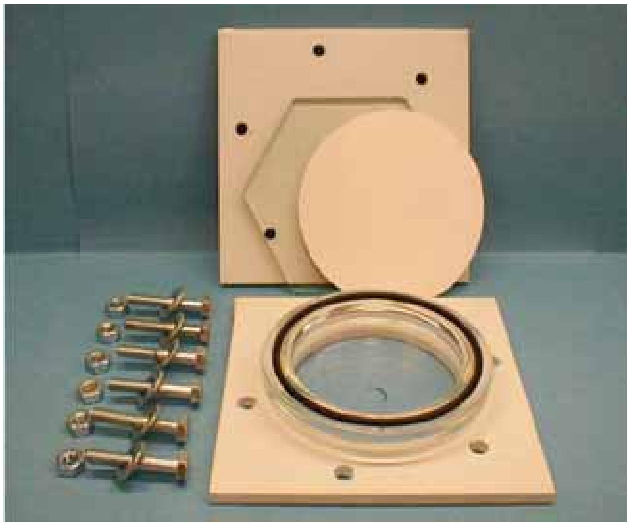

**Fig. 2. Configurations of the absorption cell.**

to predict the diffusion profile of d-limonene in the package using experimentally determined diffusion parameters and a diffusion model.

## Materials and Methods

### Packaging materials

A 180-mL cup was formed from a base material (Allista Plastic Packaging Co., Muncie, IN) from an aseptic packaging machine (Benco Asepack/2, Placenza, Italy). The base material consisted of high-impact polystyrene (HIPS) as outer layer, low-density polyethylene (LDPE) as inner layer, which contacted with food (orange juice in this current study), and polyvinylidene chloride (PVDC) between as a barrier layer. The cross-sectional image of the material is exhibited in Fig. 1.

### Orange juice preparation

Orange juice (100% juice, Tropicana Products, Inc., Chicago, IL, USA) was purchased in a local grocery store. To prevent oxidation and microbial spoilage by yeast and mold, 0.5% (v/v) of butylated hydroxyanisole (BHA) (Sigma, Louis, MO, USA) and 0.5% (v/v) of sodium benzoate (Sigma) were added, respectively.

### Absorption cell

An absorption cell was used to get flavor compounds absorbed into the multi-layered packaging material (Fig. 2). Only one side of packaging material surface was allowed to contact orange juice in the absorption cell. The absorption cell is in a circular disk shape and has a diameter of 7.5 cm and a height of 1.0 cm. Forty-three mL orange juice was filled into the cell to hold the surface/volume ratio to 1.04, simulating a 250 mL orange juice package (Sheung et al, 2004). A glass layer was placed on the top of a packaging film to block the permeation of flavor compounds. A Viton O-ring (American Packing & Gasket Co., Houston, TX, USA) was put on the top of the test cell for hermetic seal.

### d-limonene analysis

Orange juice was placed in the absorption cell and contacted with the HIPS/PVDC/LDPE packaging material for 0, 5, 12, 16, 24, 36, 48, 60, and 72 hr in an incubator at 22$^{o}$C. After incubation, the flavor-absorbed packaging materials were hung in the atmosphere (35±5% RH) for 1 hr to dry juice residues at their surfaces. Eight pieces (0.5 cm×0.5 cm) from the flavor-absorbed packaging material were placed in a 20 mL gas tight bottle. The bottle was sealed with Teflon coated rubber septa and aluminum caps (Supelco, Inc., Bellefonte, PA, USA) and incubated for 0, 0.5, 1, 2, 3, and 4 hr at 50, 60, and 70$^{o}$C for flavor desorption from the pieces of the packaging material. The desorbed volatile compounds in the headspace of the bottle were isolated by a SPME fiber with 100 mm polydimethylsiloxane (PDMS) coating, which was manually inserted into the headspace of the bottle and kept for 20 min (Fig. 3). The SPME fiber was retracted from the bottle and injected into a GC injection port at 220$^{o}$C and kept for 2 min for the desorption of volatile compounds. The desorbed flavor compounds were separated by a Hewlett-Packard 5890 GC equipped with a capillary column (30 m×0.53 mm I.D.) coated with a 2.65 mm film of 5% phenyl substituted methylpolysiloxane and a flame ionization detector. The standard calibration curve of d-limonene was obtained by plotting the GC peak area

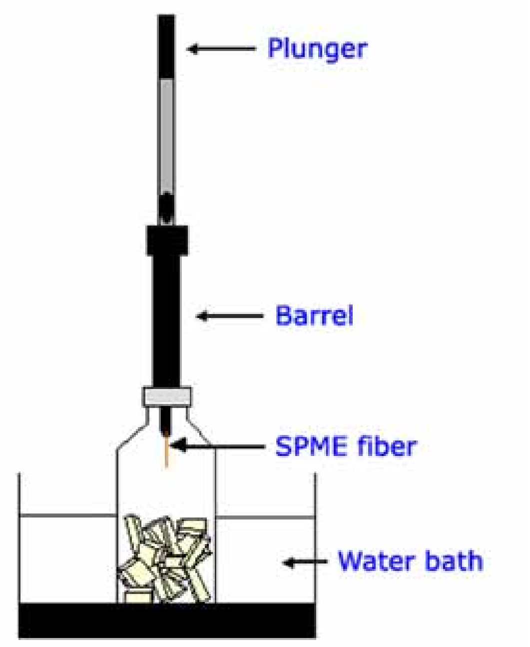

**Fig. 3. Diagram for the isolation of flavor compounds absorbed in the HIPS/PVDC/LDPE multi-layered film by SPME.**

against the know concentrations (10-500,000 ppm(w/v)) of standard d-limonene purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Four flavor-absorbed packaging materials were sampled and analyzed at each time of sampling.

### Diffusion coefficient determination

The diffusion coefficient (D) of d-limonene through the 1.5-mm thick HIPS/PVDC/LDPE multi-layered film was determined from the data obtained using a relationship derived from the solution to Fick's law for a plane sheet (Crank, 1975).

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\{-D(2n+1)^2\pi^2 t/4l^2\} \qquad (1)$$

where $M_t$ is the amount of d-limonene absorbed by the film at time t; and $M_\infty$ ($M_{inf}$) is the amount of d-limonene absorbed by the film at equilibrium; l = thickness of film.

The absorption profile of d-limonene from the film was obtained with the determined D value using Eq. (1). Fitting was done using a nonlinear function from Matlab (Version 7.1.0.246 (R14), The Mathworks Inc., Natick, MA, USA). The predicted profile by the model (Eq. (2)) was compared to that from the experimental data.

The D value was also determined by a lag time method (Eq. (2)) (Floros & Chinnan, 1989). When the concentration value ratios ($M_t/M_{inf}$) are plotted against time, over a sufficiently long time allows the calculation of D from the Eq. (2).

$$D = L^2 / 6\theta \qquad (2)$$

where L is the film thickness and θ is the lag time.

### Partition coefficient determination

The partition coefficient (K) was calculated for d-limonene. K was determined by the following equation (Nielsen et al., 1992).

$$K = \frac{[C_p]}{[C_j]} \qquad (3)$$

where $C_p$ is the concentration of d-limonene in the film and $C_j$ is the concentration of d-limonene in orange juice in a sorption cell, kept for 3 days at 23±2°C.

## Results and Discussion

### d-Limonene analysis

The concentrations of recovered d-limonene at different desorption temperature and time are exhibited in Fig. 4. The coefficients of variation of quadruplicate analyses for total absorbed volatile compounds and d-limonene were 2.5% and 3.5%, respectively. The highest concentration of d-limonene and the smallest standard deviation on the mean value of the concentration were obtained with desorption temperature of 60°C and desorption time of 1 hr.

### Diffusion coefficient

The lag time chosen to determine D using Eq. (1) was 6 hr, based on the concentration profile (Fig. 5). The D values for the

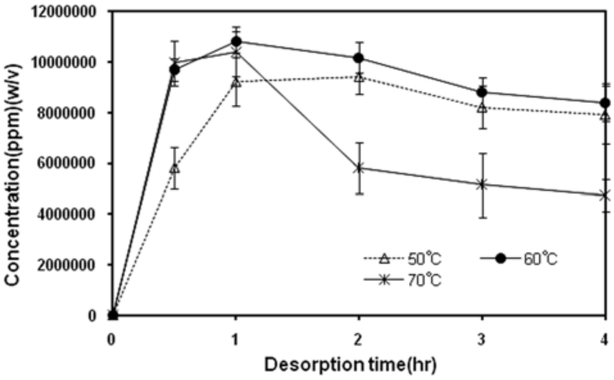

**Fig. 4. Effects of temperature and time on the desorption of d-limonene from the HIPS/PVDC/LDPE multi-layer film.**

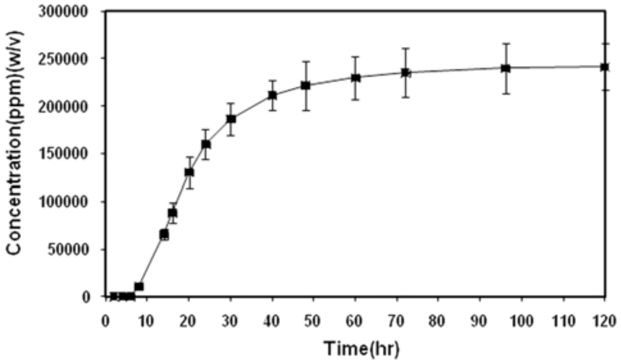

**Fig. 5. Concentration of d-limonene absorbed in the HIPS/PVDC/LDPE multi-layered film for 120 hr.**

diffusion of d-limonene through the film at 23±2°C determined by Eq. (1) and Eq. (2) were $1.73\pm0.56\times10^{-11}$ $m^2/s$ and $1.16\pm0.32\times10^{-11}$ $m^2/s$, respectively. The D values from Eqs. (1) and (2) were compared to validate the correctness of the computer model. The values from two different ways were not significantly different ($p>0.05$). The absorption profiles of d-limonene obtained from the experiment and the model (Eq. (1)) is illustrated in Fig. 6. The result from the model fitting indicated that the model did not fit the data at earlier time (<30 hr). However, the absorption data no earlier than 30 hr were well fit by the model.

### Partition coefficient

The K of d-limonene on the film was 0.03, which is similar to that of Co-PET film with a thickness of 0.07 mm (K=0.03) (Imai et al., 1990). The smaller the K, the lower the affinity of d-limonene for the polymer was (Imai et al., 1990). The K of d-limonene on the 0.127-mm PVC film was reported as 15 (Fayoux et al., 2007). The difference in the K values is probably due to the different polarities of the tested materials.

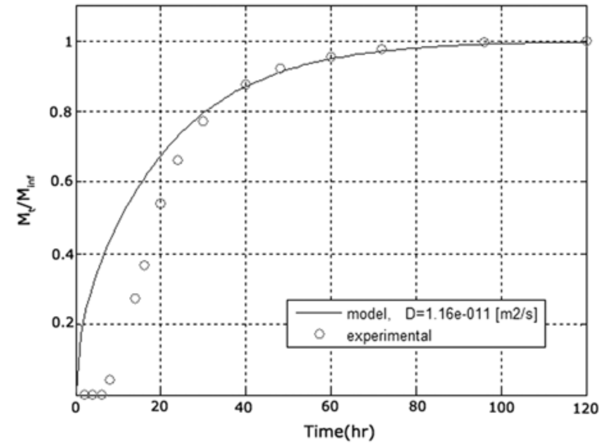

**Fig. 6. The absorption of d-limonene from the HIPS/PVDC/LDPE multi-layered film. Data obtained from the experiment and the model (Eq.(1)) are shown in ○ and ──, respectively.**

## Conclusions

A headspace SPME gas chromatography (SPME-GC) method has been developed for analysis of d-limonene absorbed in a multi-layered packaging material. The SPME was a simple, reproducible and sensitive method for the analysis of d-limonene absorbed in the packaging materials. The mathematical solution (Fig. 1) was considered useful for predicting absorption profiles, especially at earlier times of absorption and valid for determining the D value, which was confirmed by the lag time method. The method and protocols developed from the research for detecting the concentrations of d-limonene and predicting the diffusion profile of the volatile compound in the package would be useful for food guality assessment and product development.

## Acknowledgement

This work was supported by a special research grant from Seoul Women's University (2010).

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