SHORT COMMUNICATIONS

An Apparatus for Measuring the Gas Permeability of Films

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Abstract

The gas permeability of plastic films is important in packaging, containment, and agricultural fumigation. Recently, an approach for estimating the mass transfer coefficient of vapors across a film was presented by Papiernik et al. (2001). The mass transfer coefficient is an intrinsic property of a film–chemical combination, independent of the concentration gradient maintained across the film. Here we describe an apparatus useful for obtaining permeability data; the model of Papiernik et al. (2001) may be fitted to the data to determine mass transfer coefficients. The assembled equipment provides a sealed permeability cell, where a sample of the film to be tested is sandwiched between two static half-cells. Vapor is spiked to one side of the film and the concentrations in the spiked and receiving chamber are monitored until equilibrium. A sealed system is required for this approach; the permeability cells described here were gas-tight for >40 d. This approach produces reproducible measures of mass transfer coefficients that are not dependent on the size of the experimental apparatus. Model parameters were similar when fitted simultaneously as when determined independently from the same data set.

PLASTIC films are used in a wide variety of applications for exclusion or containment of water vapor and other gases. The permeability of plastic films to gases is of particular concern in food packaging (for permeability to oxygen, ethylene, and flavor components, for example) and in agricultural fumigation (for containment of fumigant compounds). Historically, the gas permeability of films has been determined by measuring the flux of compound traversing the film in a flow-through chamber (Kolbezen and Abu-El-Haj, 1977; Daponte, 1995; Gamliel et al., 1998), or by pressurizing a chamber and monitoring the change in pressure or volume in a second chamber on the opposite side of the film (Anonymous, 1992; Gamliel et al., 1998). These methods produce a measure of permeability that is dependent on the concentration gradient maintained across the film. Papiernik et al. (2001) presented a method for determining the permeability of plastic films that is independent of the concentration gradient. This method uses a sealed static chamber to monitor gas diffusion across a film membrane. The mass transfer coefficient that results from the analysis is a property of the film–chemical combination that changes only with environmental conditions (i.e., temperature). Here, we provide a detailed description of an apparatus suitable for the

measurement of mass transfer coefficients according to the method of Papiernik et al. (2001).

Materials and Methods

General Method

A closed, sealed cell is constructed such that a sample of the film to be tested is held between two chambers. The chemical to be evaluated is spiked in the gas phase to one side of the film (source chamber). The chemical diffusion through the film is monitored by measuring the decrease in concentration in the source chamber and the accompanying increase in concentration on the opposite side of the film (the receiving chamber). The concentration data are required for estimating the mass transfer coefficient (h) via the method of Papiernik et al. (2001).

Construction of the Permeability Cells

Cells were prepared in two sizes, because the diffusive path length affects the time required for the system to come to equilibrium. The cells were constructed of 127-mm (5 in.)-outside diameter × 120.5-mm (4.75 in.)-inside diameter 304 stainless steel cylindrical stock. Rings were cut from this stock: 40 mm in length for the large cells (Fig. 1A) and 10 mm in length for the small cells (Fig. 1B). The steel rings were soldered to 152-mm (6 in.) squares of 0.9-mm (0.037 in.)-thick stainless steel sheet metal (Fig. 1C). The faces of the rings were smoothed and trued using a metal lathe to ensure a precise fit when the two half-cells were assembled together and also to standardize the cell volumes.

In the large cells, sampling ports were installed in the cylindrical wall 15 mm above the base plate. A threaded 5-mm hole was drilled through the cell wall to accept the sampling port. Sampling ports (Fig. 1D) were constructed of brass unions (1/16-in. tube × 1/16-in. tube), installed from the outside, and the threads of each union were sealed with slow-set epoxy. A brass nut (1/16-in. tube) was modified by threading the outside to 5/16-in. UNF thread. Teflon-faced silicone septa (4 mm diam. × 3 mm thick, punched from larger septa) were placed inside the nuts and the nuts threaded onto the unions, sealing the threads with slow-set epoxy. Because gas-tight syringes were used to collect samples, puncturing the septum with the syringe needle with each sample collected, it was necessary to additionally seal the ports between sampling times so that there was no leakage from the septa, which were punctured multiple times. For this purpose, plastic caps with 5/16-in. UNF interior threads (to fit on the exterior of the brass threaded nuts) were fitted with teflon-faced silicone septa (7 mm diam. × 3 mm thick), placed over a plastic disk (7 mm diam. × 1 mm thick). One sampling port was installed in the receiving chamber. Two ports were installed 180° from

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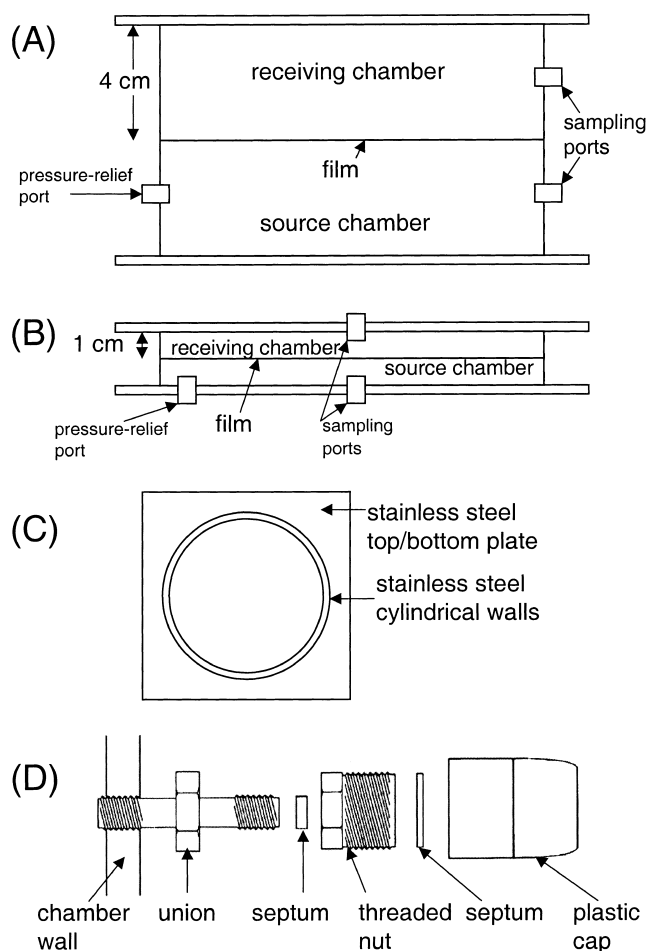**Abbreviations:** HDPE, high density polyethylene.

Fig. 1. Cells used for permeability testing. (A) Large cells, where each chamber is 40 mm in length; (B) small cells, where each chamber is 10 mm in length; (C) cross-section of cell; and (D) construction of ports.

each other in the source chamber. A needle was placed in the second port of the source chamber (puncturing the septum) to relieve the pressure during the injection process to avoid pressurizing the cell.

For the small cells, a 5-mm (13/64 in.) hole was drilled through the sheet metal base and brass 10-32 nuts were soldered over the outside face of the holes to provide a larger threaded surface to receive the brass union ports. All other components of the sampling ports were the same as in the larger cells. Sampling ports were centered in each half-cell and an additional port was installed about 10 mm from the edge of the ring in the source chamber for pressure relief.

Film Testing

The cells were used to measure the mass transfer of dichloromethane vapor through 1.0-mil high density polyethylene (HDPE), Parafilm-M (American National Can, Menasha, WI; thickness 5.5 mil), and 0.5-mil Saran (S.C. Johnson, Racine, WI). Each film to be tested was sandwiched between one source cell and one receiving cell (Fig. 1A and B); triplicate cells were used for each test. The film was secured to each cell half with epoxy and adhesive aluminum tape was applied to the exterior of the assembled cell to ensure a gas-tight seal. Films were not stretched during assembly. The experiments were conducted in a controlled-temperature room at 25°C; all equipment to be used during spiking and sampling was

equilbrated at 25°C. Saturated vapor was prepared by adding 0.5 mL of liquid dichloromethane to a 150-mL vial. The vial was capped with a gas-tight seal and allowed to come to equilibrium at 25°C. A separate saturated vapor source was prepared for each cell to be spiked. Dichloromethane vapor (20 mL to large cells; 5 mL to small cells) was spiked to the source chamber of each cell with a known offset between replicates. Beginning 5 min after spiking, samples were collected from the source chamber (250 μL) and receiving chamber (500 μL) of each cell using gas-tight syringes. Samples were transferred to 10-mL headspace vials, capped immediately, and stored at −78°C until analysis. Approximately 10 sets of samples were collected from each replicate cell over the sampling period. Using this sampling scheme, removal of samples results in the removal of approximately 4% of the volume of the receiving cell and 2% of the volume of the source cell for 1-cm half-cells, and ≤1% of the volume of the 4-cm half-cells. The pressure reduction induced by sampling was monitored in replicate cells containing 1-mil HDPE. The maximum pressure drop occurred during and in the first few seconds after sampling. In the large cells, the maximum pressure change when withdrawing 500 μL from one half-cell was 5 Pa, and the maximum pressure decrease when sampling 250 μL was 2.2 Pa. In the small cells, the maximum pressure decrease when withdrawing 500 μL from one half-cell was 19 Pa; a maximum pressure change of 8 Pa was recorded when withdrawing 250 μL.

Data Analysis

A detailed description of the model used to determine mass transfer coefficients is given in Papiernik et al. (2001). Briefly, the assembled permeability cell is considered as a two-layer system separated by a membrane that impedes diffusion and is sorptive to the spiked compound. The analytical solution for the concentration in each chamber when the source chamber has an initial concentration of C_0 and the length of both chambers is the same ($L_s = L_r = L$) is:

$$C_r(t) = \frac{C_0 L}{2} \left[\frac{L + k_p \exp\left(\dfrac{-\alpha(k_p + L)t}{L}\right)}{L(k_p + L)} \right.$$

$$+ \frac{2h + \alpha(k_p - L) - \sqrt{\beta}}{2L\sqrt{\beta}}$$

$$\exp\left(\frac{-(2h + \alpha(k_p + L) - \sqrt{\beta})t}{2L}\right)$$

$$- \frac{2h + \alpha(k_p - L) + \sqrt{\beta}}{2L\sqrt{\beta}}$$

$$\left. \exp\left(\frac{-(2h + \alpha(k_p + L) + \sqrt{\beta})t}{2L}\right) \right] \qquad [1]$$

for the receiving chamber and:

$$C_s(t) = \frac{C_0 L}{2} \left[\frac{L + k_p \exp\left(\dfrac{-\alpha(k_p + L)t}{L}\right)}{L(k_p + L)} \right.$$

$$- \frac{2h + \alpha(k_p - L) - \sqrt{\beta}}{2L\sqrt{\beta}}$$

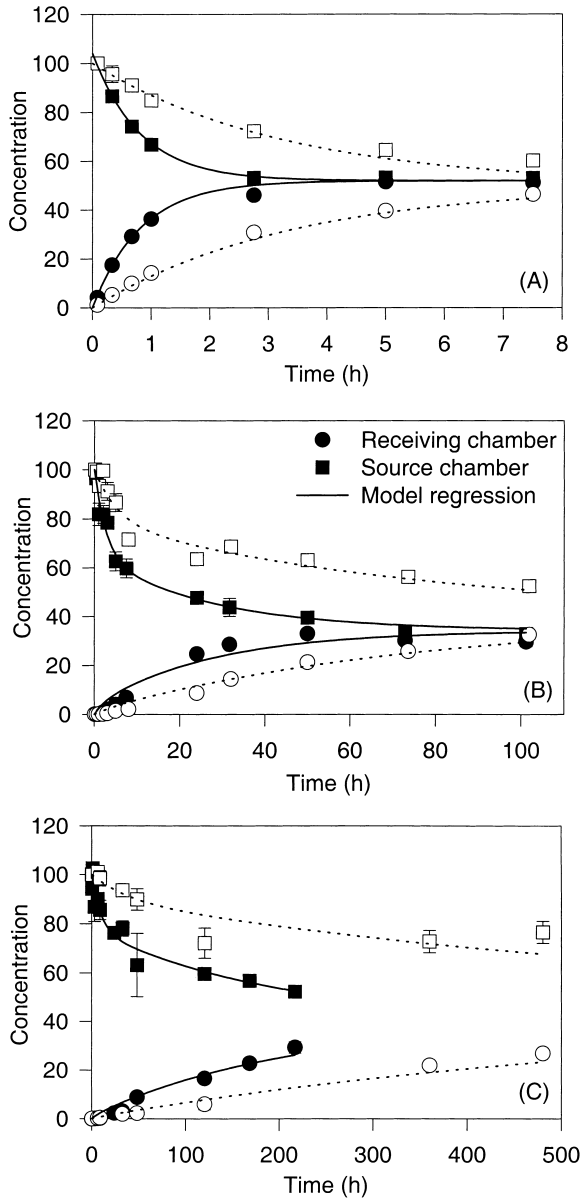$$\exp\left(\frac{-(2h + \alpha(k_p + L) - \sqrt{\beta})t}{2L}\right)$$

Fig. 2. Experimental data and model regression for dichloromethane diffusing through (*A*) high density polyethylene (HDPE); (*B*) Parafilm-M; and (*C*) Saran at 25°C. Solid symbols and lines are for small cells; open symbols and dotted lines are for large cells.

Table 1. Values for the mass transfer coefficient (*h*), system equilibrium kinetic parameter (α), and equilibrium sorption coefficient (*k*$_p$) for dichloromethane transport through various films at 25°C. Values in parentheses are from independent determination using Eq. 4 and 5.

Parameter	Large cells (*L* = 4 cm)	Small cells (*L* = 1 cm)
1-mil HDPE†		
h, cm h^{-1}	0.60 ± 0.03	0.61 ± 0.02
Parafilm-M		
h, cm h^{-1}	0.032 ± 0.003	0.028 ± 0.003
	(0.033 ± 0.003)	(0.026 ± 0.004)
α, h^{-1}	0.15 ± 0.05	0.25 ± 0.06
	(0.46)	(0.24)
k$_p$, cm	1.0 ± 0.1	0.46 ± 0.04
	(0.70)	(0.60)
Saran		
h, cm h^{-1}	0.0033 ± 0.0005	0.0032 ± 0.0003
	(0.0034 ± 0.0005)	(0.0033 ± 0.0003)
α, h^{-1}	0.02 ± 0.03	0.08 ± 0.03
	(0.09)	(0.09)
k$_p$, cm	0.4 ± 0.2	0.27 ± 0.03
	(0.22)	(0.23)

† HDPE = high density polyethylene. No significant sorption to this film. Regression for determination of *h* fixed α and *k*$_p$ at 10^{-6}. Independent fitting of α and *k*$_p$ was not appropriate with indeterminable sorption.

by the ratio $k_p = S_s(\infty)/C_s(\infty) \equiv S_r(\infty)/C_r(\infty)$ and α [t^{-1}] is the system-equilibrium adsorption rate parameter. A minimization algorithm is used to simultaneously determine *h*, α, and *k*$_p$.

Alternatively, the parameters may be determined independently for each data set (Papiernik et al., 2001). The equilibrium adsorption coefficient was calculated as:

$$k_p = L\left(\frac{C_0 - 2C_{s,\infty}}{2C_{s,\infty}}\right) \quad [4]$$

where $C_{s,\infty}$ was estimated as the mean of the source and receiving cell concentrations in the final samples. The system kinetic parameter was determined as:

$$\alpha = \frac{-L\left(\dfrac{dC_r}{dt} + \dfrac{dC_s}{dt}\right)}{k_p} \quad [5]$$

and approximated by considering the change in concentration with time immediately after spiking (the first two data points) in the source and receiving cells. Fixing the values of C_0, α, and k_p allowed for a regression with a single adjustable parameter, *h*.

Results and Discussion

Data and model fits are shown in Fig. 2. The gas-phase concentration in the source cell is depleted as the concentration in the receiving cell increases. For Parafilm-M and Saran, equilibrium concentrations were less than 50% of the initial source concentration because the films are sorptive to organic vapors (Papiernik et al., 1999, 2001). No sorption of dichloromethane was observed to HDPE. The model produced a good fit to the data for all films, which had widely varying mass transfer characteristics (Fig. 2).

The cells were gas-tight, showing no evidence of leakage in cells incubated for >40 d (Papiernik et al., 2001). Experiments using the same film in both the small cells

$$+ \frac{2h + \alpha(k_p - L) + \sqrt{\beta}}{2L\sqrt{\beta}}$$

$$\exp\left(\frac{-(2h + \alpha(k_p + L) + \sqrt{\beta})t}{2L}\right)\Bigg] \quad [2]$$

for the source chamber where $\beta = -8hL\alpha + [2h + \alpha(k_p + L)]^2$. The mass transfer coefficient is *h* and has units L t^{-1}. Adsorption to the film is modeled as a kinetic process at early times that approaches equilibrium at later times:

$$\frac{\partial S}{\partial t} = \alpha[k_p C(t) - S(t)] \quad [3]$$

where *S* is the mass of adsorbed chemical per film area [M L^{-2}], k_p [L] is the equilibrium adsorption coefficient defined

and large cells produced the same mass transfer coefficient (Table 1). Use of the small cells is advantageous in testing relatively impermeable films, because the time required for the system to achieve equilibrium is reduced as a result of the shorter diffusion path length (Fig. 2).

Parameter estimation was accomplished by nonlinear regression allowing h, α, and k_p to vary simultaneously, and also by independent determination using long-time behavior to approximate k_p and early-time behavior to determine α, then fixing these values and using the model to determine h only. Both approaches produced very similar values for all three parameters for each data set (Table 1). Other means of obtaining these parameters are not applicable to the system used in these experiments: the parameter α is dependent on numerous factors including system geometry, rate of diffusion to the film surface, and sorption kinetics. Equilibrium determinations of sorption (for example, those of Papiernik et al., 1999) may not be directly applicable to the parameter k_p because of the long times allowed for equilibrium in the permeability cells and because film edge effects may be important.

Permeability cells of this type are relatively easy to construct and very simple to use to determine mass transfer coefficients. Care must be taken to ensure that the stainless steel surfaces are smooth and true, because minor surface flaws can result in significant leakage. Cells should be tested for gas-tightness before use. Pressure testing and long-term incubations using an impermeable film are recommended. We used stainless steel and epoxy in the construction of these cells to minimize interactions between the compound being tested and the cells themselves; material compatibility should be verified before cells are constructed.

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