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## PERMEATION OF NITROGEN AND OXYGEN INTO POLYMER GAS-SAMPLING BAGS

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### SUMMARY

An expression is derived for the rate of change in gas concentration within a polymer bag caused by permeation through the walls of gases from the surrounding air. The rates of permeation of nitrogen and oxygen into such bags have been measured by gas chromatography and fitted to the theoretical expression to give an estimate of the permeation coefficients. These coefficients are compared with known values for the polymers involved. The significance of the results is discussed with regard to the purity of samples stored in gas-sampling bags.

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### INTRODUCTION

Gas-sampling bags constructed of various polymers are commonly used in the determination of volatile components in air. The bags are used both for collection of samples in the field and for assay calibration and validation in the laboratory. Since the mixtures typically consist of low concentrations in air of the compounds of interest, the permeability of a bag towards these components is of primary concern, and the materials of construction are chosen accordingly. However, in some instances the bulk contents of the bag differ significantly from the surrounding air. For example, it is sometimes convenient to use a bag to store a pure organic vapor for convenience in handling. It may also be desirable to prepare ppm-level mixtures in pure nitrogen to avoid problems caused by exposure to oxygen. In such cases, the permeability of the bag walls to atmospheric oxygen and nitrogen becomes of potential significance.

The permeability of polymers to a variety of gases has been extensively studied and tabulated<sup>1</sup>. Although permeation rates through polymer films are typically measured by determination of the pressure or volume changes that result, gas chromatography (GC) has been used for analysis in systems involving mixed vapors<sup>2</sup>. Similarly, the recognition of chromatographic disturbances caused by diffusion through PTFE sample loops<sup>3</sup> led to the use of such a system for measurement of the permeability of polymer tubing towards oxygen and nitrogen<sup>4</sup>. However, the significance of these permeation constants with respect to the integrity of a sample within a gas bag has not generally been considered. In the course of GC studies of atmospheres within the bag different from air, we became aware of the speed of dilution of

the contents through permeation of nitrogen and oxygen. A study was begun to determine the rate of this process for some of the commonly available gas-sampling bags.

## THEORY

The permeation rate of a gas through a polymer film is usually described by an expression in the form of eqn. 1 (refs 1, 5), where  $V$  is the net volume (at STP) of gas that has passed through the film,  $t$  is the elapsed time.  $P_H$  and  $P_L$  are the partial pressures of the gas on the high- and low-pressure sides of the membrane, respectively.  $A$  and  $l$  are the area and thickness of the membrane, and  $Q$  is the permeability coefficient.

$$\frac{dV}{dt} = QA \frac{(P_H - P_L)}{l} \quad (1)$$

For a gas-sampling bag filled with an inert component and immersed in air, it is convenient to replace  $P_H$  and  $P_L$  by the corresponding mole fractions ( $X_H$  and  $X_L$ ) multiplied by the pressure of the atmosphere,  $P$ . If it is assumed that  $P$  is constant, the instantaneous rate of permeation of nitrogen or oxygen into the bag is given by eqn. 2, where  $K$  is a constant. For the solution of eqn. 2, the simplifying assumption was made of a mixture of two gases, one of which permeates through the walls of the bag while the other does not. If the bag is filled initially with a volume  $V_0$  of a mixture with mole fraction  $X_0$  of the permeating component and immersed in a gas with corresponding mole fraction  $X_H$ , the time required for a given volume of this component to enter the bag is given by eqn. 3, where  $A$  is the surface area of the bag.

$$\frac{dV}{dt} = \frac{QAP}{l} (X_H - X_L) = KA(X_H - X_L) \quad (2)$$

$$\frac{1}{(X_H - 1)^2} \left\{ V(X_H - 1) + V_0 (X_0 - 1) \ln \left[ 1 + \frac{V(X_H - 1)}{V_0(X_H - X_0)} \right] \right\} = KA t \quad (3)$$

Equation 3 was used as the model to fit the data for diffusion of nitrogen and oxygen into bags constructed from different polymers.

## EXPERIMENTAL

### Instrumentation

A Varian Model 3700 gas chromatograph equipped with a thermal-conductivity detector was used for the analysis. The gases were separated on a stainless-steel column (6 ft.  $\times$  1/8 in.) packed with 5A molecular sieves and run at ambient temperature, with helium as the carrier gas. Samples of 0.5 ml were injected with a gas-tight syringe. Peak-area determinations and calculations were carried out by a Hewlett-Packard Model 3354 data system. For the mixtures containing only nitrogen and oxygen, quantitation was done by normalization, referenced to ambient air. For

TABLE I  
CHARACTERISTICS OF GAS-SAMPLING BAGS STUDIED

Bags	Material of construction	Dimensions (cm)	Surface area (cm <sup>2</sup> )	Supplier
A	Teflon FEP, Type A, 0.005 in.	30.5 × 30.5	1720	Alltech Associates, Inc.
B	Teflon FEP, 0.005 in.	35 × 35	2710	
B'	Teflon FEP, 0.005 in.		2810	Pollution Measurement Corp.
C	Tedlar, 0.002 in.		2900	
C'	Tedlar, 0.002 in.		2900	
D	Multilayer	20 × 38 (snout-shape)	1180	Calibrated Instruments, Incl.

mixtures containing Freon 12, the nitrogen peak was quantitated by the external-standard method.

The pertinent data about the gas-sampling bags studied are summarized in Table I. The bags were obtained from commercial suppliers and were formed from two flat pieces sealed at the edges. The surface areas were calculated from measurements of the deflated bags. All bags were equipped with septa for sample withdrawal.

### Analysis

The zero-time gas was metered into the bag to be tested by means of a 1-l gas syringe, and GC analysis was carried out immediately to verify the composition. The bag was then suspended in the laboratory from a clamp attached to one edge, to ensure that all surfaces were accessible to diffusion. The chromatographic determination was repeated at intervals over a period of 10–12 days.

### RESULTS

In the initial experiments, the bags were filled with nitrogen, and the increase in oxygen concentration with time was determined (Table II). The volume of oxygen entering a bag in each time period was calculated from the concentration change

TABLE II  
PERMEATION OF NITROGEN AND OXYGEN INTO GAS-SAMPLING BAGS

Bag	Initial contents	Time dependence of composition									
A	N <sub>2</sub> , 3000 ml	Time (h)	0	4.23	5.68	22.4	28.9	98.0	149.7	263.7	
		O <sub>2</sub> (%)	0.202	0.302	0.969	2.64	3.24	9.06	11.9	16.3	
B	N <sub>2</sub> , 4000 ml	Time (h)	0	4.25	6.00	22.5	29.1	98.2	150.1	263.8	
		O <sub>2</sub> (%)	0.097	0.696	0.897	2.88	3.59	10.2	12.7	16.7	
C	N <sub>2</sub> , 4000 ml	Time (h)	0	4.23	5.85	22.4	29.1	98.1	149.9	263.8	
		O <sub>2</sub> (%)	0.081	0.232	0.302	0.752	1.01	2.97	3.23	6.65	
D	N <sub>2</sub> , 1000 ml	Time (h)	0	5.77	76.0	240.5					
		O <sub>2</sub> (%)	0.470	0.551	1.88	5.18					
B'	Freon 12, 4000 ml	Time (h)	0	5.70	76.0	126.4	240.5				
		N <sub>2</sub> (%)	2.47	3.33	12.7	17.5	25.7				
C'	Freon 12, 4000 ml	Time (h)	0	5.48	76.2	240.7					
		N <sub>2</sub> (%)	0.48	0.77	5.40	14.7					

under the assumption that the volume of nitrogen did not change. This assumption was justified both by the observation that nitrogen permeation rates are smaller than those of oxygen for most polymers<sup>1</sup> and by the fact that permeation of a small volume of nitrogen out of the bag would have a negligible effect on its concentration, at least at the shorter times. The volumes thus calculated were fitted by trial and error to eqn. 3 to give an initial estimate for the constant  $K$ . However, it was recognized that the assumption of no nitrogen permeation leads to systematic over-estimation of the volumes and of  $K$ .

To improve the accuracy of the model, a second series of measurements was carried out for bags B' and C', which are duplicates of B and C. The bags were filled with Freon 12, and the rate of increase in nitrogen concentration was determined. In principle, the oxygen permeation rate could also be checked in this experiment, but the oxygen and Freon 12 did not separate under the GC conditions used. The volume of oxygen entering during each period was therefore estimated from equation 3 with the approximate constants obtained in the first experiments, and the calculated total gas volume was increased by this amount. The Freon 12 was assumed not to permeate the bag walls at a significant rate. The nitrogen volumes thus calculated were fitted to eqn. 3 to determine the nitrogen permeation coefficient. In an iterative process, this coefficient was used in turn to estimate the amount of nitrogen leaving the bag during each time interval in the initial experiments and to calculate corrected

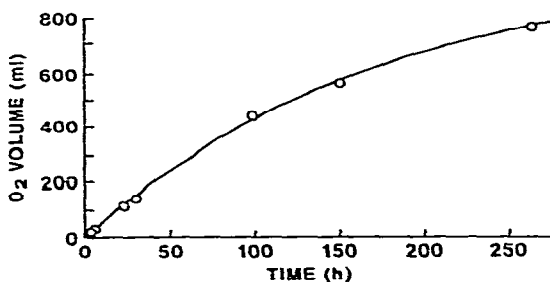
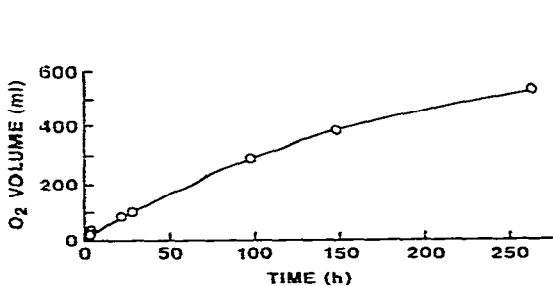


Fig. 1. Volume of oxygen diffusing into bag A as a function of time, with fitted curve for eqn. 3;  $K = 1.10 \cdot 10^{-2} \text{ ml/cm}^2 \cdot \text{h}$ .

Fig. 2. Same as Fig. 1 for bag B;  $K = 1.10 \cdot 10^{-2} \text{ ml/cm}^2 \cdot \text{h}$ .

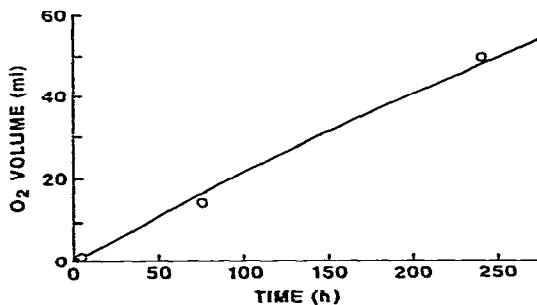
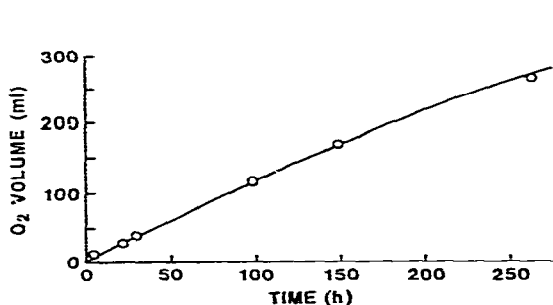


Fig. 3. Same as Fig. 1 for bag C;  $K = 2.08 \cdot 10^{-3} \text{ ml/cm}^2 \cdot \text{h}$ .

Fig. 4. Same as Fig. 1 for bag D;  $K = 9.3 \cdot 10^{-4} \text{ ml/cm}^2 \cdot \text{h}$ .

oxygen volumes and the corresponding permeation coefficients. The nitrogen permeability measured for bag B' was also used to calculate the volume corrections for bag A. No nitrogen permeability was determined for bag D, but because of the low oxygen permeability, the error is estimated to be less than 5% in this instance. The volume of oxygen entering the bags as a function of time is plotted in Figs. 1-4, along with the "best-fit" curves for eqn. 3.

## DISCUSSION

The values of  $K$  corresponding to the curves in Figs. 1-4 are given in Table III. For comparison of these constants with literature permeabilities, it is necessary to correct the units, noting from eqn. 2 that, in the standard units,  $Q = Kl/P$ . It is further necessary to correct the volume terms to standard conditions. In this correction, the average temperature and pressure were assumed to be 25°C and 750 mmHg, respectively. The resulting constants are given as  $Q$  in Table III. This Table shows that the oxygen constants obtained for Teflon bags A and B are identical, even though the bags were of different dimensions and from different manufacturers. The constants are also in good agreement with those from the literature. This establishes the validity of the experimental model used, and it shows that the permeability of the bag walls is a sufficient explanation of the observed changes in concentration.

TABLE III

CALCULATED PERMEABILITIES OF GAS-SAMPLING BAGS COMPARED WITH LITERATURE VALUES

Values of  $Q$  are in centibarrers: 1 centibarrer =  $\frac{10^{-12} \text{ cm}^3 \text{ (STP)} \cdot \text{cm}}{\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}}$

Bag	Material	$K(\text{ml}/\text{cm}^2 \cdot \text{h})$		$Q$		$Q$ from literature
		$O_2$	$N_2$	$O_2$	$N_2$	
A	Teflon	0.0110		468		539*, 450**
B	Teflon	0.0110				
B'	Teflon		0.00365		155	208*, 192**
C	Tedlar	0.00208		35.4		2.0*, 1.9**
C'	Tedlar		0.00138		23.5	0.42*, 0.15**
D	Multilayer	0.00093				

\* From ref. 1, average value.

\*\* DuPont Company, private communication.

The agreement of the calculated constants  $Q$  with literature values for the Tedlar bags is much worse, well outside the experimental error. Not only are the nitrogen and oxygen rates individually high by 20- to 50-fold, but the oxygen/nitrogen ratio (usually diagnostic for the polymer type) is much too low. The reasons for this discrepancy are not clear, but it may be that, with the lower intrinsic permeabilities, other factors (such as leakage of the bags) become more significant. Because the walls of bag D were formed from several layers of unknown composition and thickness, a permeability constant in standard units could not be calculated for it, but, as

indicated by the manufacturer, it showed the lowest permeability towards oxygen of the set. However, it is interesting that the permeability is only lower by a factor of *ca.* 2 than that of the 2-mil Tedlar and is, in fact, greater than that expected for Tedlar from the literature constants. Leaks may also play a role in bag D, but, because of its considerably different size and shape, the importance of this factor would probably be different than for the other bags.

It is clear from these results that gas-sampling bags, especially those constructed of Teflon, must be used with care if significant errors due to permeability of the walls are to be avoided. For the nominal 5-l Teflon bag filled with 4 l of a gas other than air, a dilution of *ca.* 3% with oxygen and 5% with nitrogen will occur in 24 h. Thus, in 1 day, the composition would change enough to cause a significant error in a GC calibration. Further, a bag filled initially with a pure organic vapor may produce a combustible mixture by admitting sufficient oxygen. These permeation rates should be considered in any application involving storage of samples in gas-sampling bags.

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