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Analysis of Mathematical Models of Integrating Monitoring Devices

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Final Report Covering the Period
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U.S. DEPARTMENT OF COMMERCE, Philip M. Klutznick, ***Secretary***
Luther H. Hodges, Jr., ***Deputy Secretary***
Jordan J. Baruch, ***Assistant Secretary for Science and Technology***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

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Preface

The work reported here on analyzing the efficiency of models of personal monitoring devices was supported by the Office of Air and Water Measurement of NBS. The work was completed in 1976, but not reported in detail. Since that time, interest in such personal monitoring devices has continued to increase (see References 13-16). In addition, a group at NBS, which includes Dr. Jimmie A. Hodgeson, is presently undertaking a study of such devices. Dr. Hodgeson has encouraged the preparation and publication of this report.

1. INTRODUCTION

In this paper we analyze two mathematical models of a personal monitoring device. The purpose of the device, which is to be worn by an individual, is to indicate the level of exposure to various criteria air pollutants such as O_3, SO_2, NO_2, CO during a time period which might range from 24 hours to a week or longer. The goal of the analysis of the models is to determine how the quantity of pollutant which is collected is related to the average pollutant concentration and how material constants such as solubility and diffusion coefficients affect the operation of the device.

The first model consists of a pollutant-permeable membrane exposed to the atmosphere and backed by a reactive substrate which serves to trap any pollutant that has diffused through the membrane. The quantity of pollutant collected is related to the parameters of the model which in this case are: solubility coefficient of the pollutant gas in the membrane, diffusion coefficient of the pollutant gas in the membrane, membrane thickness, and the pollutant gas partial pressure as a function of the time. Our analysis of this simple model (Model I) has led us to consider a second model (Model II) in which the reactive substrate is replaced by reactive sites which are distributed uniformly throughout the membrane. Model 1 is treated in Section 2 and Model II is treated in Section 3. The collecting efficiencies of these models are compared in Section 4 for "typical" values of material parameters. We conclude there that the efficiency of Model II is superior to that of Model I.

2. ANALYSIS OF BADGE MONITOR MODEL I

The first model of a badge monitor which we consider consists of a permeable membrane exposed to ambient air on one side and backed by a reactive substrate on the other. When the monitor is exposed to air containing some time-varying amount of a criteria air pollutant (e.g. O_3, SO_2, NO_2, CO), the pollutant can diffuse through the membrane and subsequently react with or be trapped on the reactive substrate. In Model I, we assume that the transport of the pollutant through the membrane is adequately described by the one-dimensional diffusion equation:

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}, \tag{1}$$

where $c(x,t)$ is the concentration of the dissolved pollutant in the membrane at position x and time t expressed in the units, moles per unit volume. The one-dimensional configuration for Model I is shown in Fig. 1. The membrane lies between the surfaces at $x=0$ and $x=l$, the latter surface being the one exposed to the air and to a time varying partial pressure of pollutant, $p(t)$. The boundary conditions which the solution of Eq. (1) is assumed to satisfy at the surfaces $x=0$ and $x=l$ are:

(i) at $x=l$, there must be equilibrium between the pollutant in the gas phase and the pollutant dissolved in the membrane at $x=l$

$$c(l,t) = S\,p(t). \tag{2}$$

In Eq. (2) S is the solubility coefficient of the pollutant in the membrane expressed in the same concentration units as $c(x,t)$ per unit pressure. Since we are interested in small partial pressures and low concentrations, we have assumed the simplest form for the solubility relation in Eq. (2).

(ii) at $x=0$, there is a similar condition. Since the substrate is assumed to react or trap the gas leaving the membrane, the condition equivalent to Eq. (2) is[1]

$$C(0,t)=0. \tag{3}$$

In the initial condition, or state, of the membrane, the concentration of dissolved gas is identically zero,

$$C(x,0)=0, \quad 0\le x\le \ell. \tag{4}$$

The solution of Eq. (1) with the boundary conditions (2) and (3) for the initial condition (4) is[2]

$$C(x,t)=\frac{2D\pi}{\ell^2}\sum_{n=1}^{\infty} n \, \exp\left(-\frac{Dn^2\pi^2 t}{\ell^2}\right)\sin\left(\frac{n\pi x}{\ell}\right) \times \int_0^t (-1)^{n+1} S p(\lambda)\exp\left(\frac{Dn^2\pi^2\lambda}{\ell^2}\right)d\lambda. \tag{5}$$

The transport, or flux of dissolved gas from right to left across the plane surface at x in Fig. 1 is given by the expression

$$F(x,t)= D\,\frac{\partial C(x,t)}{\partial x}, \tag{6}$$

where $F(x,t)$ is the flux of gas molecules measured in moles per unit area per unit time.

The total flux across the surface $x=0$ into the reactive substrate during the time interval $0<t\le T$ is

$$\begin{aligned}\Phi(T)&=\int_0^T F(0,t)\,dt\\ &=D\int_0^T \left.\frac{\partial C(x,t)}{\partial x}\right|_{x=0} dt,\end{aligned} \tag{7}$$

where the time T corresponds to the total time of exposure to the pollutant. The explicit relation between $\Phi(T)$ and $p(t)$ can be obtained by substituting Eq. (5) in Eq. (7) and carrying out the indicated operations. The final result is (see Appendix A for details)

$$\Phi(T) = \frac{DS}{\ell}\int_0^T p(t)\,dt - 2\frac{DS}{\ell}\sum_{n=1}^{\infty}(-1)^{n+1}\int_0^T p(T-t)\exp\left(\frac{-Dn^2\pi^2 t}{\ell^2}\right)dt \,. \tag{8}$$

It is also shown in Appendix A that in the expected mode of operation of the monitor, the expression for the total amount of pollutant collected in the substrate is given by the first term alone in Eq. (8)

$$\Phi(T) = \frac{DS}{\ell}\int_0^T p(t)\,dt \tag{9}$$

or

$$\Phi(T) = \frac{DS}{\ell}\,\bar{p}\,T \tag{10}$$

where $\bar{p}$ is the average partial pressure of the pollutant during the time T,

$$\bar{p} = \frac{1}{T}\int_0^T p(t)\,dt. \tag{11}$$

The error, $\mathcal{E}$, which is made by neglecting the second term in Eq. (8),

$$\mathcal{E} = \left| \Phi(T) - \frac{DS}{\ell} \int_0^T p(t)\,dt \right| , \tag{12}$$

is shown to be less than

$$\frac{DSp_m}{\ell} \frac{\ell^2}{3D} \tag{13}$$

where p_m is the maximum value of $p(t)$. By comparing the expression for the error in Eq. (13) with the total amount of pollutant collected in the substrate (10), it is seen that the error $\mathcal{E}$ is certainly negligible if $T \gg \ell^2/D$ when $\bar{p} \sim p_m$. The characteristic time ℓ^2/D is the longest relaxation time associated with transient concentration distributions in the membrane. In fact, the expression for the total flux in Eq. (9) can be derived by assuming that at each instant there is a uniform concentration gradient equal to $S p(t)/\ell$.

Thus the integrating or averaging characteristics of this model of a badge monitor is extremely simple. The total amount of pollutant collected, according to Eqs. (9) and (10) is proportional to the time integral of the partial pressure during the operating period T. In choosing a membrane material for the monitor, the product DS, which is called the permeability, should be as large as possible and the membrane thickness as small as possible. Typical values of these material parameters will be discussed further in Section 4.

3. ANALYSIS OF BADGE MONITOR MODEL II

In analyzing Model I in Section 2, we found that the membrane should be as thin as possible. That is, the sensitivity of the monitor becomes greater the closer the reactive substrate is to the exposed surface. Clearly there is a practical limit, with decreasing membrane thickness, at which the membrane becomes too fragile. For this reason, we consider the modified badge monitor Model II where, instead of a reactive substrate, reactive sites are distributed uniformly throughout the bulk of the membrane material. In this way, trapping sites are brought as close as possible to the exposed surface of the membrane. The one-dimensional configuration for Model II is shown in Fig. 2. The membrane again lies between the surfaces at $x=0$ and $x=\ell$, the latter surface being the one exposed to the air and a time varying partial pressure of pollutant, $p(t)$. In our analysis we assume, for simplicity, that the surface at $x=0$ is impermeable to gas diffusing in the membrane. If both surfaces were exposed to the pollutant, i.e., if the exposed surface area were doubled, then the amount of trapped pollutant would be approximately doubled. In Model II, we assume that the transport of the pollutant through the membrane is described by the modified diffusion equation:

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2} - k\,c(x,t)\,n(x,t) \tag{14}$$

and the companion equation

$$\frac{\partial n(x,t)}{\partial t} = -k\,c(x,t)\,n(x,t), \tag{15}$$

where $C(x,t)$ is the concentration of the untrapped or unreacted gas at position x and time t, $n(x,t)$ denotes the concentration of trapping sites at position x and time t, D is the diffusion coefficient of the unreacted gas assumed to be independent of the extent of the chemical reaction. It is evident from the form of Eq. (15) that the chemical reaction involving the trapping sites is assumed to be bimolecular and irreversible; and k is the rate constant of the reaction. The boundary conditions, which the concentration $C(x,t)$ is assumed to satisfy at the surfaces $x=0$ and $x=\ell$, are:

(i) at $x=\ell$, there is equilibrium between the pollutant in the gas phase and the unreacted pollutant dissolved in the membrane

$$c(l,t) = S\,p(t). \tag{16}$$

In Eq. (16) it is assumed that the solubility constant of the gas in the membrane is independent of the extent of the reaction between the gas and the reactive sites. (ii) at $x=0$, the condition of impermeability is equivalent to the requirement that the flux of unreacted gas across the $x=0$ plane is zero, so

$$\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=0} = 0. \tag{17}$$

As with Model I, the initial concentration of pollutant dissolved in the membrane is assumed to be zero,

$$c(x,0) = 0\,, \quad 0 \leqslant x \leqslant l. \tag{18}$$

The initial concentration of reactive sites (which are immobile) is assumed to be uniform,

$$n(x,0) = n_0\,, \quad 0 \leqslant x \leqslant l. \tag{19}$$

Eqs. (14) and (15) are nonlinear; and although these equations have been discussed in a number of different contexts,[2,3,4,5] a general solution for the boundary and initial conditions (16)-(19) has not been obtained. However, a number of exact solutions and approximate solutions have been obtained in various limiting cases. We now consider some of these special cases.

(3.1) Limiting Case IIA

In the first case, we assume that the initial concentration of trapping sites, n_o , is so large compared to, $Sp(t)$, the concentration of dissolved pollutant gas at the exposed surface, that $n(x,t)$ remains approximately unchanged during the period of operation of the monitor. The diffusion equation (14) is effectively linearized

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2} - k n_o c(x,t). \tag{20}$$

The foregoing reduction has been proposed by several investigators[6]. The solution of Eq. (20) with the boundary conditions (16) and (17) and the initial condition (18) is[7]

$$\begin{aligned} c(x,t) = \frac{2D\pi}{l^2}\sum_{m=0}^{\infty}(m+\tfrac{1}{2})\exp\{-[kn_o+(m+\tfrac{1}{2})^2\pi^2 D l^{-2}]t\}\cos[(m+\tfrac{1}{2})\tfrac{\pi x}{l}] \times \\ \int_0^t (-1)^m S p(\lambda)\exp\{[kn_o+(m+\tfrac{1}{2})^2\pi^2 D l^{-2}]\lambda\}\,d\lambda. \end{aligned} \tag{21}$$

Eq. (21) is an expression for the local concentration of dissolved pollutant which has not reacted. In order to obtain the expression for the total amount of pollutant which has reacted up to time T , first integrate both sides of Eq. (20) with respect to x between the limits 0 and l to obtain

$$\frac{\partial C(t)}{\partial t} = D\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=l} - k n_o C(t) \tag{22}$$

where

$$C(t) = \int_0^{\ell} c(x,t)\,dx \tag{23}$$

is the total amount of unreacted gas in the membrane at time t per unit surface area of the membrane. Then integrate both sides of Eq. (22) from 0 to T and rearrange terms to give the following expression for the total flux of pollutant entering the membrane during the time interval $0 < t \leq T$ (per unit surface area of the membrane)

$$D\int_0^T \left.\frac{\partial c(x,t)}{\partial x}\right|_{x=\ell} dt = C(T) + kn_o\int_0^T C(t)\,dt. \tag{24}$$

Clearly Eq. (24) is a simple statement of conservation of molecules; and the total amount of pollutant which has reacted up to time T is the second term on the right-hand side of Eq. (24),

$$R(T) = kn_o\int_0^T C(t)\,dt. \tag{25}$$

Combining Eqs. (21), (23) and (25), one obtains (see Appendix B)

$$R(T) = \frac{DS}{\ell}\int_0^T p(t)\,dt\left[\ell\left(\frac{kn_o}{D}\right)^{1/2}\right]\tanh\left[\ell\left(\frac{kn_o}{D}\right)^{1/2}\right] - 2\frac{DS}{\ell}\sum_{m=1}^{\infty}\left[D\pi^2(m+\tfrac{1}{2})^2\ell^{-2} + kn_o\right]^{-1}\times \int_0^T p(T-t)\exp\left\{-\left[D\pi^2(m+\tfrac{1}{2})^2\ell^{-2} + kn_o\right]t\right\}dt. \tag{26}$$

As in the case of Model I, the first term on the right-hand side of Eq. (26) is the dominant part of $R(T)$,

$$R(T) = \frac{DS}{\ell}\int_0^T p(t)\,dt\left[\ell\left(\frac{kn_0}{D}\right)^{1/2}\right]\tanh\left[\ell\left(\frac{kn_0}{D}\right)^{1/2}\right]. \tag{27}$$

If the relaxation time for diffusion, ℓ^2/D, is much smaller than the relaxation time for reaction, $(kn_0)^{-1}$, then the expression for $R(T)$ in Eq. (27) reduces to

$$R(T) \cong \ell k n_0 S \int_0^T p(t)\,dt, \qquad kn_0\ell^2/D \ll 1, \tag{28}$$

a result independent of D, as should be expected. If we compare the amount of pollutant collected in Model II, Eq. (27), with that collected in Model I, Eq. (9), it is seen that the ratio

$$\frac{R(T)}{\Phi(T)} = \left(\frac{kn_0\ell^2}{D}\right)^{1/2}\tanh\left[\left(\frac{kn_0\ell^2}{D}\right)^{1/2}\right], \tag{29}$$

can, in principle, exceed unity when $kn_0\ell^2/D > 1$. Whether the assumptions on which Eq. (27) is based and whether either of the inequalities, $kn_0\ell^2/D \ll 1$ or $kn_0\ell^2/D > 1$, can be satisfied in practice is discussed further in Section 4.

(3.2) Limiting Case IIB

We next drop the assumption that the concentration of trapping sites is unchanged and consider the solution of Eqs. (14) and (15) in the limit where the rate of diffusion is very rapid compared to the rate of chemical reaction. This limiting condition was introduced in obtaining Eq. (28) for $R(T)$. If the relaxation time for diffusion is short compared to the relaxation time for chemical reaction, and short compared to the time scale on which the partial pressure of pollutant varies, then the concentration of dissolved pollutant is constant throughout the membrane

$$C(x,t) = S p(t) , \qquad 0 \leq x \leq \ell .$$

Thus, in Eq. (15) there is no dependence of $n(x,t)$ on x and the solution of Eq. (15) is

$$n(T) = n_o \exp\left(-kS\int_0^T p(t)dt\right). \tag{30}$$

The total amount of pollutant gas which has reacted with trapping sites in the time interval 0 to T is

$$\begin{aligned} R(T) &= \ell\left[n_o - n(T)\right] \\ &= \ell n_o\left[1 - \exp\left(-kS\int_0^T p(t)dt\right)\right]. \end{aligned} \tag{31}$$

Clearly, the approximate expression for $R(T)$ in Eq. (28) can be obtained from Eq. (31) if the exponent in (31) is small compared to unity.

(3.3) Limiting Case IIC

Now consider the opposite extreme to case (b) in which the trapping reaction can be treated as instantaneous on the time scale of the diffusion process. Since the reaction is treated as instantaneous, dissolved gas and trapping sites cannot both be present in the same volume element of the membrane. Therefore, there is a region next to the exposed surface in which all trapping sites are filled and in which additional pollutant gas is free to diffuse. This region is separated from virgin membrane by a sharp plane boundary which moves at a velocity determined by the rate at which dissolved pollutant gas diffuses to the moving boundary. Hermans[8] has formulated the equations of motion of this moving boundary problem and obtained a solution in the case where the partial pressure of the gas is constant at the exposed surface. The diagrammatic representation adopted by Hermans is shown in Fig. 3. A constant concentration of the diffusing pollutant is maintained at $x = 0$,

$$c(0,t) = Sp_0 \,, \quad t \geqslant 0.$$

From this point, the concentration decreases and becomes zero at a point ξ. The slope of the C-x curve at this point is determined by the condition

$$-D \frac{\partial c}{\partial x}\bigg|_{x=\xi} = n_0 \frac{d\xi}{dt}. \tag{32}$$

The left-hand side of Eq. (32) specifies the number of moles of dissolved gas molecules diffusing to ξ per unit area per unit time and the right-hand side is the flux of molecules required per unit area per unit time to fill the trapping sites as the boundary point ξ moves to the right. The boundary condition (32) can be transformed to

$$D\left(\frac{\partial c}{\partial x}\bigg|_{x=\xi}\right)^2 = n_0 \frac{\partial c}{\partial t}\bigg|_{x=\xi} \tag{33}$$

because

$$\frac{\partial c}{\partial x}\bigg|_{x=\xi} d\xi + \frac{\partial c}{\partial t}\bigg|_{x=\xi} dt = 0. \tag{34}$$

Consequently, Eqs. (14) and (15) with the appropriate boundary conditions and initial equations have been replaced in the present limiting case by the simple diffusion equation

$$\frac{\partial c(x,t)}{\partial x} = D \frac{\partial^2 c(x,t)}{\partial x^2} \,, \quad 0 \leqslant x \leqslant \xi \tag{35}$$

with the boundary conditions

$$c(0,t) = Sp_0 \,, \tag{36}$$

$$c(\xi,t) = 0 \,, \tag{37}$$

and

$$D\left(\frac{\partial c}{\partial x}\bigg|_{x=\xi}\right)^2 = n_\circ \frac{\partial c}{\partial t}\bigg|_{x=\xi} , \tag{38}$$

and the initial condition

$$c(x,0) = 0 , \quad 0 < x . \tag{39}$$

Hermans[8] shows that the solution to this problem is

$$c(x,t) = S p_\circ \left[1 - \frac{G(x[4Dt]^{-1/2})}{G(\xi[4Dt]^{-1/2})} \right] , \tag{40}$$

where

$$G(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-s^2} ds . \tag{41}$$

In Eq. (40) the quantity,

$$z = \xi [4Dt]^{-1/2} , \tag{42}$$

is a constant which is determined by the transcendental equation,

$$z e^{z^2} G(z) = \pi^{-1/2} n_\circ^{-1} S p_\circ . \tag{43}$$

Thus the position coordinate, ξ, of the moving boundary increases proportional to the square root of the time, according to Eq. (42); and the constant, z, depends on the constant $\pi^{-1/2} n_\circ^{-1/2} S p_\circ$ as shown in Fig. 4. For small values of $n_0^{-1} S p_0$, Eq. (43) reduces to

$$z \cong (S p_0 / 2 n_0)^{1/2}, \tag{44}$$

or

$$\xi \cong (2 S p_0 D t / n_0)^{1/2}. \tag{45}$$

Having determined the position of the moving boundary point ξ as a function of the time t, we have also determined the total quantity of gas trapped in the membrane at time t under the constant partial pressure exposure condition (36),

$$R(t) = n_0 \xi. \tag{46}$$

In the limit of small $S p_0 / n_0$, (46) is simply

$$R(t) \cong (2 S p_0 D t \, n_0)^{1/2}. \tag{47}$$

The approximate expression Eq. (45) for the position of the interface was obtained in the limit where $S p_0 / n_0$ is small compared to unity. It should also be recalled that the exact solution from which (45) was obtained strictly applies only if the partial pressure in the gas phase is a constant. Clearly, this limitation of constant partial pressure of the pollutant is overly restrictive for the application we have in mind. In order to assess the integrating characteristics of Model II when there is a time varying partial pressure, we have two approaches available. First, we could undertake the numerical solution of

Eqs. (35), (37) and (39) for a "typical" partial pressure history $p(t)$ and compare the position of the interface at time T with that obtained from Eqs. (42) and (43) when the assumed constant partial pressure p_0 is the average.

$$p_0 = \frac{1}{T}\int_0^T p(t)\,dt.$$

Rather than develop this approach here, we adopt a second approach which involves the approximate solution of Eqs. (35), (37) and (39). The remainder of this section is devoted to summarizing the physical nature of the approximation which was apparently first used by Mott and Gurney[9] in the case where the partial pressure in the gas phase is constant.

Mott and Gurney assume that in Eq. (32) the concentration gradient is linear over the whole range $0 \le x \le \xi$, i.e.,

$$c(x,t) = S p_0 \left(1 - \frac{x}{\xi}\right) \tag{48}$$

so that Eq. (32) can be replaced by

$$\xi \frac{d\xi}{dt} = DSp_0/n_0 \tag{49}$$

or

$$\xi = (2DSp_0 t/n_0)^{1/2}, \tag{50}$$

a result obtained in Eq. (45) by assuming that $Sp_0 n_0^{-1}$ is small compared to unity. Booth[10] had made the point that although Eq. (48) is not exact, it is approximately correct. Furthermore, he has shown that the error made in using (48) is small provided that

$$Sp_0 n_0^{-1} \ll 1. \tag{51}$$

This last condition is equivalent to the requirement that the concentration of the diffusing gas is small compared to the concentration of trapping sites. Physically this requirement can be understood in terms of the following form of Eq. (32)

$$n_o \, d\xi = -D \left.\frac{\partial c}{\partial x}\right|_{x=\xi} dt \, . \tag{52}$$

In the time interval dt, the diffusive flux of gas molecules is $-D \left.\frac{\partial c}{\partial x}\right|_{x=\xi} dt$, and the boundary moves through a distance $d\xi$ which is inversely proportional to n_o. Thus for larger relative values of n_o, the boundary moves slower and there is more time to establish the "steady-state" concentration distribution (48). We propose that this argument can be carried one step further and that the same approximation can be used when the partial pressure is time-dependent, namely

$$c(x,t) = S\,p(t)\left(1 - \frac{x}{\xi}\right) \tag{53}$$

and,

$$\xi \frac{d\xi}{dt} = DS\,p(t)/n_o \tag{54}$$

for $S\,p(t)/n_o << 1$.

The expression for the position of the boundary which is obtained by integrating Eq. (54) is

$$\xi = \left[2DS \int_0^t p(\tau)\,d\tau \,/n_o\right]^{1/2} . \tag{55}$$

Ultimately, the validity of the approximate expression for ξ in Eq. (55) can be assessed by numerical integration. For the present, we will use Eq. (55) to determine the total amount of gas trapped in the membrane (per unit area) in the time interval 0 to T

$$R(T) = n_0 \xi$$

or

$$R(T) = \left[2DSn_0 \int_0^T p(t)\,dt\right]^{1/2}. \tag{56}$$

According to Eq. (56), the collecting efficiency of badge monitor Model II is optimized by choosing materials for which DS and n_0 are as large as possible. Typical values of these material parameters are given in Section 4.

4. CHARACTERISTICS OF MODELS I AND II

The performance characteristics of Model I are summarized in Eq. (9) and (10).

$$\Phi(T) = Q\ell^{-1}\int_0^T p(t)\,dt \tag{9}$$

$$= Q\ell^{-1}T\bar{p} \tag{10}$$

where $\Phi(T)$ is the number of moles of pollutant trapped in the time interval T seconds in the substrate backing of a square centimeter of membrane ℓ centimeters thick. The permeability, $Q = DS$, of the membrane is measured in the units: moles, cm (thickness) per second per square centimeter of membrane area per atmosphere of pressure difference across the membrane; and the time-dependent partial pressure, $p(t)$, of the pollutant gas is measured in atmospheres. There are two significant aspects of the expression for $\Phi(T)$ in Eq. (9). First, the integrating characteristics of the model are ideally simple, i.e., the amount of pollutant collected is simply proportional to the time integral of the partial pressure of the pollutant. This time integral in turn is expressible as an average partial pressure, $\bar{p}$, multiplied by the time interval T,

$$\int_0^T p(t)\,dt = T\bar{p}.$$

The absolute amount of pollutant gas collected is controlled by the magnitude of the coefficient $Q\ell^{-1}$ in Eq. (9). In order to estimate the value of $\Phi(T)$, we refer to a recent compilation of permeabilities, Q_{HCK} , by Hwang, Choi, and Kammermeyer.[11] In that reference, the permeability units of Q_{HCK} are: cm^3 of gas at S.T.P., cm (thickness) per second per square centimeter of membrane area per cm of Hg pressure difference across the membrane. In terms of Q_{HCK}, the expression in Eq. (10) is

$$\Phi(T) = Q_{HCK}\frac{76}{22400}\ell^{-1}T\bar{p}.$$

The expression for the number of moles collected in one day of exposure to an average partial pressure of the pollutant of 5 x 10^{-8} atm (which is the maximum allowable value of 50 ppb) is then

$$\begin{aligned}\Phi^{(max)} &= Q_{HCK}\,\frac{76}{22400}\,\ell^{-1}(86400)(5\times10^{-8}) \\ &\cong \underset{\wedge}{\overbrace{}^{Q_{HCK}}} 1.47\times10^{-5}\,\ell^{-1}\ \text{moles/cm}^2\end{aligned} \tag{57}$$

Typical values of Q_{HCK} lie in the range

$$10^{-10} \text{ to } 10^{-8}$$

for gases such as N_2, O_2, CO_2, CH_4. If we assume this range of values to be typical for the criteria pollutants, then $\Phi^{(max)}$ lies in the range

$$1.5\times10^{-15}\,\ell^{-1} \quad \text{to} \quad 1.5\times10^{-13}\,\ell^{-1}\ \text{moles/cm}^2. \tag{58}$$

It was noted in analysing Model I in Section 2 that the value of $\Phi(T)$ was inversely proportional to the thickness of the membrane. For that reason, we considered a second model, Model II, in which the effective membrane thickness was reduced to the greatest extent possible. In section 3, several approximate expressions were obtained for R(T), the number of moles of pollutant trapped per square centimeter of membrane in the case of Model II. We confine our attention to the result in Eq. (56),

$$R(T) = \left[2Qn_0\int_0^T p(t)\,dt\right]^{1/2} \tag{56}$$

or

$$= \left[2Qn_0T\bar{p}\right]^{1/2} \tag{59}$$

where definitions of quantities in (56) and (59) are the same as in Eqs. (9) and (10) and where n_0 is the concentration of trapping sites in moles per cm^3. We now calculate for R(T), an expression analogous to $\Phi^{(max)}$ in Eq. (57). In the case of

Model II, Eq. (59), the expression for the number of moles of gas collected in one day of exposure to an average partial pressure of pollutant of 5×10^{-8} atm is

$$R^{(max)} = \left[2 Q_{HCK} \frac{76}{22400}(86400)(5\times10^{-8})\, n_o\right]^{1/2}.$$

For values of Q_{HCK} in the range

$$10^{-10} \text{ to } 10^{-8}$$

the range of values for $R^{(max)}$ is

$$5.4\times10^{-8}\, n_o^{1/2} \qquad \text{to} \qquad 5.4\times10^{-7}\, n_o^{1/2} \quad \text{moles/cm}^2. \tag{60}$$

In the most favorable circumstances, the largest value of n_o which might be achieved is of the order 10^{-2} moles/cm^3. Thus the range of values for $R^{(max)}$ in (60) is considerably more favorable than the range of values of $\Phi^{(max)}$ in Eq. (58). It should be noted that in the version of Model II which lead to the formula for $\dot{R}(T)$ in Eqs. (56) and (59) we succeeded in reducing the effective "thickness" of the membrane. This "effective" thickness is given by Eq. (55) the formula for the position ξ of the interface at time T

$$\xi = \left[2 Q n_o^{-1} \int_0^T p(t)\, dt\right]^{1/2}. \tag{55}$$

The range of values of the "thickness", ξ, which corresponds to the range in $R^{(max)}$ in Eq. (60) is

$$5.4\times10^{-8}\, n_o^{-1/2} \qquad \text{to} \qquad 5.4\times10^{-7}\, n_o^{-1/2} \quad \text{cm},$$

or

$$5.4\times10^{-7} \qquad \text{to} \qquad 5.4\times10^{-6} \quad \text{cm} \qquad \text{if}$$

n_o is as large as 10^{-2}.

APPENDIX A. DERIVATION OF EXPRESSION FOR Φ(T) IN EQ. (8).

The total flux in the time interval $(0,T)$ in moles per unit area across the surface at $x=0$ is given in Eq. (7)

$$\Phi(T) = D\int_0^T \left.\frac{\partial c(x,t)}{\partial x}\right|_{x=0} dt \tag{A1}$$

where

$$c(x,t) = \frac{2D\pi}{\ell^2}\sum_{n=1}^{\infty} n e^{-Dn^2\pi t/\ell^2} \sin\left(\frac{n\pi x}{\ell}\right)\int_0^t e^{Dn^2\pi^2\lambda/\ell^2}(-1)^{n+1} S p(\lambda)\, d\lambda. \tag{A2}$$

In order to avoid the formal divergence of series when (A2) is substituted in (A1), we proceed in the following manner. First, calculate

$$\int_0^t c(x,t)\,dt = \frac{2D\pi}{\ell^2}\sum_{n=1}^{\infty}\int_0^T n e^{-Dn^2\pi^2 t/\ell^2}\sin\left(\frac{n\pi x}{\ell}\right)\int_0^t e^{Dn^2\pi^2\lambda/\ell^2}(-1)^{n+1} S p(\lambda)\,d\lambda\, dt$$

by integrating by parts, and obtain

$$\int_0^T c(x,t)\,dt = \frac{2D\pi}{\ell^2}\left\{\sum_{n=1}^{\infty} n \sin\left(\frac{n\pi x}{\ell}\right)\left[\frac{e^{-Dn^2\pi^2 t/\ell^2}}{-Dn^2\pi^2/\ell^2}\int_0^t e^{Dn^2\pi^2\lambda/\ell^2}(-1)^{n+1} S p(\lambda)\,d\lambda\right|_0^T + \frac{\ell^2}{Dn^2\pi^2}\int_0^T (-1)^{n+1} S p(t)\,dt\right\}$$

$$= \frac{2}{\pi} S \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\sin\left(\frac{m\pi x}{\ell}\right)\left\{\int_0^T p(t)\,dt - \int_0^T p(t) e^{-\frac{Dn^2\pi^2}{\ell^2}(T-t)}\,dt\right\}. \tag{A3}$$

The series which multiplies $\int_0^T p(t)\,dt$ in Eq. (A3) has the value

$$\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\sin\left(\frac{n\pi x}{\ell}\right) = \frac{\pi}{2}\frac{x}{\ell} \quad , \quad -\ell < x < \ell \quad ; \tag{A4}$$

so the expression for $\int_0^t c(x,t)\,dt$ reduces to

$$\int_0^T c(x,t)\,dt = S\frac{x}{\ell}\int_0^T p(t)\,dt - \frac{2}{\pi} S \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\sin\left(\frac{n\pi x}{\ell}\right)\int_0^T p(T-t) e^{-Dn^2\pi^2 t/\ell^2}\,dt. \tag{A5}$$

The total flux $\Phi(T)$ can now be obtained by substituting Eq. (A5) in the expression

$$\Phi(T) = D\frac{\partial}{\partial x}\left(\int_0^T c(x,t)\,dt\right)\Bigg|_{x=0} .$$

The final result is

$$\Phi(T) = \frac{DS}{\ell}\int_0^T \wp(t)dt - \frac{2}{\ell}DS\sum_{n=1}^{\infty}(-1)^{n+1}\int_0^T \wp(T-t)e^{-Dn^2\pi^2 t/\ell^2}dt. \tag{A6}$$

It is possible to obtain a crude but useful upper bound on the series in Eq. (A6) by replacing each term by its absolute value and by replacing $\wp(T-t)$ by its maximum value $\wp_m$. The result is,

$$\begin{aligned} \mathcal{S} &= \frac{2}{\ell}DS\sum_{n=1}^{\infty}(-1)^{n+1}\int_0^T \wp(T-t)e^{-Dn^2\pi^2 t/\ell^2}dt \\ &\leq \frac{2}{\ell}DS\wp_m\sum_{n=1}^{\infty}\frac{\ell^2}{Dn^2\pi^2}\left(1-e^{-Dn^2\pi T/\ell^2}\right) \\ &\leq \frac{DS\wp_m}{\ell}\,\frac{\ell^2}{3D}. \end{aligned} \tag{A7}$$

Thus the contribution of the series in Eq. (A6) to the total flux collected per square centimeter in the time interval T is at most a constant, independent of the value of T.

APPENDIX B. DERIVATION OF EXPRESSION FOR R(T) IN EQ. (26).

The total amount of gas per square centimeter which has reacted with trapping sites in the membrane in the time interval 0 to T is given in Eq. (25),

$$R(T) = k n_0 \int_0^T C(t)\,dt \tag{B1}$$

where C(t) is defined in Eq. (23)

$$C(t) = \int_0^{\ell} c(x,t)\,dx \tag{B2}$$

and the expression for $c(x,t)$ is given in Eq. (21)

$$c(x,t) = \frac{2D\pi}{\ell^2} \sum_{m=0}^{\infty} (m+\tfrac{1}{2}) e^{-\Omega_m t} \cos\left[(m+\tfrac{1}{2})\pi \frac{x}{\ell}\right] \int_0^t e^{\Omega_m \lambda} (-1)^m S\, p(\lambda)\, d\lambda \tag{B3}$$

with

$$\Omega_m = k n_0 + (m+\tfrac{1}{2})^2 \pi^2 \ell^{-2} D. \tag{B4}$$

Substitute (B3) in (B2) and perform the integration over x to obtain

$$C(t) = \frac{2DS}{\ell} \sum_{m=0}^{\infty} e^{-\Omega_m t} \int_0^t e^{\Omega_m \lambda} p(\lambda)\, d\lambda. \tag{B5}$$

Next, substitute (B5) in the expression (B1) for R(T) and integrate by parts to obtain

$$R(T) = 2\frac{k n_0 DS}{\ell} \sum_{m=0}^{\infty} \left\{ \frac{1}{\Omega_m} \int_0^T p(t)\,dt - \frac{1}{\Omega_m} \int_0^T e^{-\Omega_m (T-t)} p(t)\,dt \right\}. \tag{B6}$$

The first sum in Eq. (B6) is[12]

$$\begin{aligned}\sum_{m=0}^{\infty} \Omega_m^{-1} &= \sum_{m=0}^{\infty} \left[k n_o + (m+\tfrac{1}{2})^2 D \pi^2 \ell^{-2}\right]^{-1} \\ &= \frac{\ell}{2D}\left(\frac{k n_o}{D}\right)^{-1/2} \tanh\left[\ell\left(\frac{k n_o}{D}\right)^{1/2}\right].\end{aligned} \tag{B7}$$

Substituting (B7) in (B6), one obtains

$$\begin{aligned}R(T) = {} & \frac{DS}{\ell}\left[\ell\left(\frac{k n_o}{D}\right)^{1/2}\right] \tanh\left[\ell\left(\frac{k n_o}{D}\right)^{1/2}\right] \int_0^T p(t)\,dt \\ & -2\,\frac{k n_o D S}{\ell} \sum_{m=0} \Omega_m^{-1} \int_0^T e^{-\Omega_m t}\, p(t)\,dt\end{aligned} \tag{B8}$$

A crude upper bound can be obtained for the remaining sum in Eq. (B8) by using a similar procedure to that used in deriving Eq. (A7). Here too, the upper bound is a constant, independent of T, so that for sufficiently large values of T the second term can be neglected.

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List of Symbols

$c(x,t)$ = concentration of gas dissolved in membrane, moles cm^{-3}.

D = diffusion coefficient, cm^{2} sec^{-1}.

$p(t)$ = partial pressure of gas at time t, atm.

S = solubility coefficient of gas in membrane, moles cm^{-3} atm.$^{-1}$.

$F(x,t)$ = flux of diffusing gas, moles cm^{-2} sec^{-1}.

$\Phi(t)$ = total flux of gas diffusing into substrate in the time t, moles cm^{-2}.

ℓ = thickness of membrane, cm.

$n(x,t)$ = concentration of trapping sites at position and time t, moles cm^{-3}.

n_o = initial concentration of trapping sites, moles cm^{-3}.

k = rate constant of irreversible bi-molecular chemical reaction between diffusing gas molecules and trapping sites, moles^{-1} cm^{3} sec^{-1}.

$C(t)$ = total amount of unreacted gas per unit area in membrane at time t, moles cm^{-2}.

$R(T)$ = total amount of gas per unit area which has reacted up to time T, moles cm^{-2}.

List of Illustrations

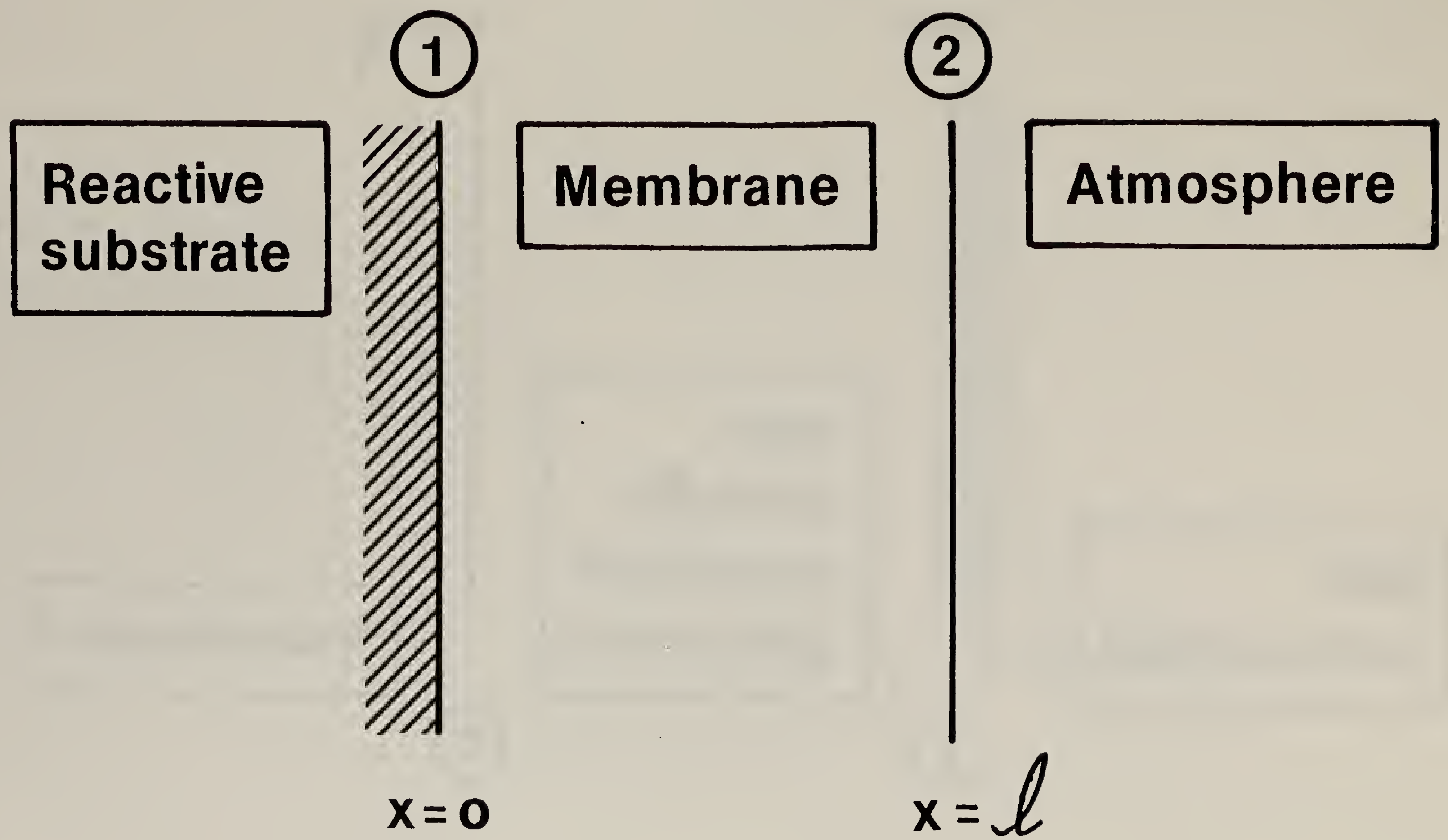


FIGURE 1

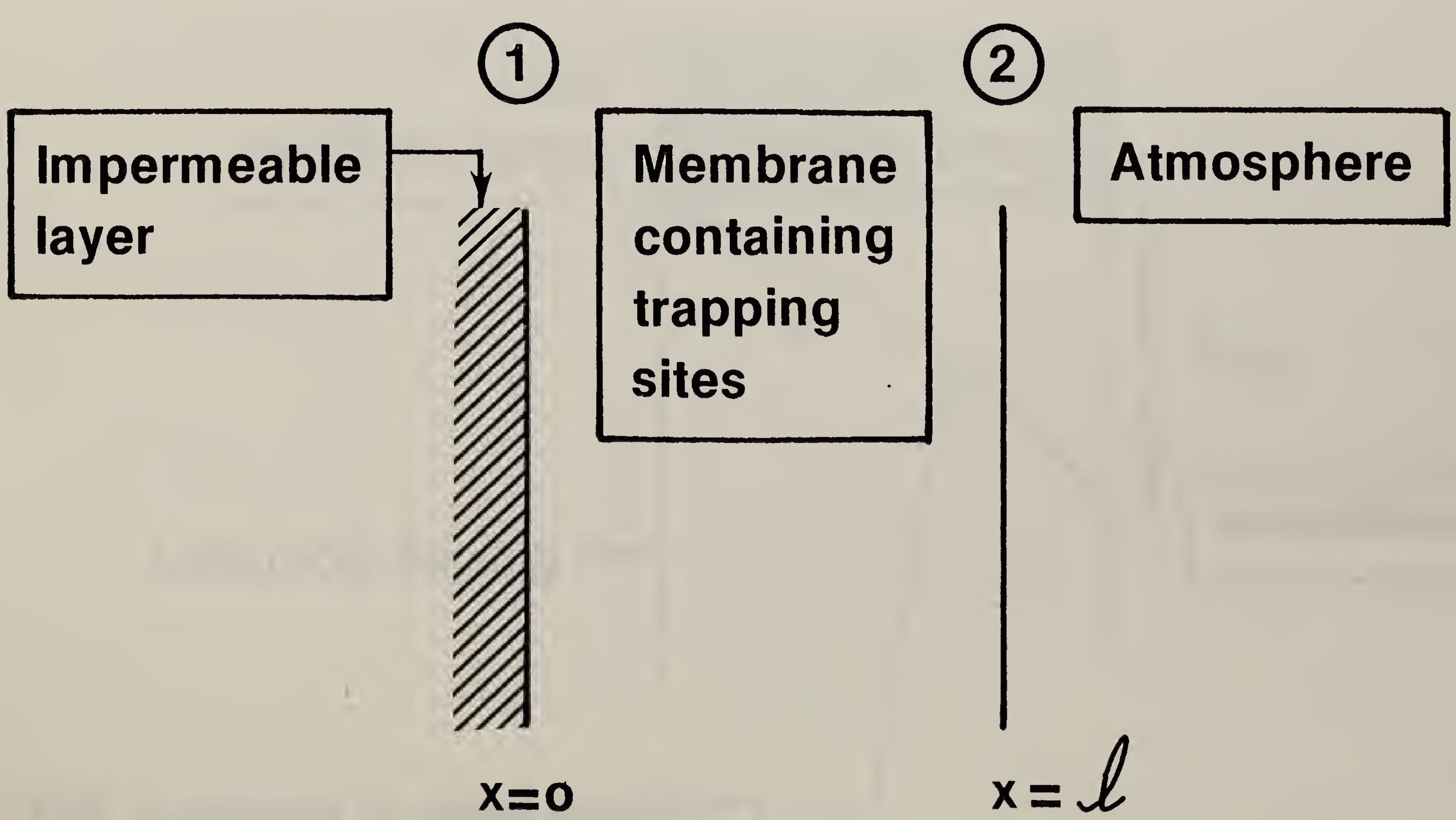

①
②
Impermeable layer
Membrane containing trapping sites
Atmosphere
x=0
x = ℓ

FIGURE 2

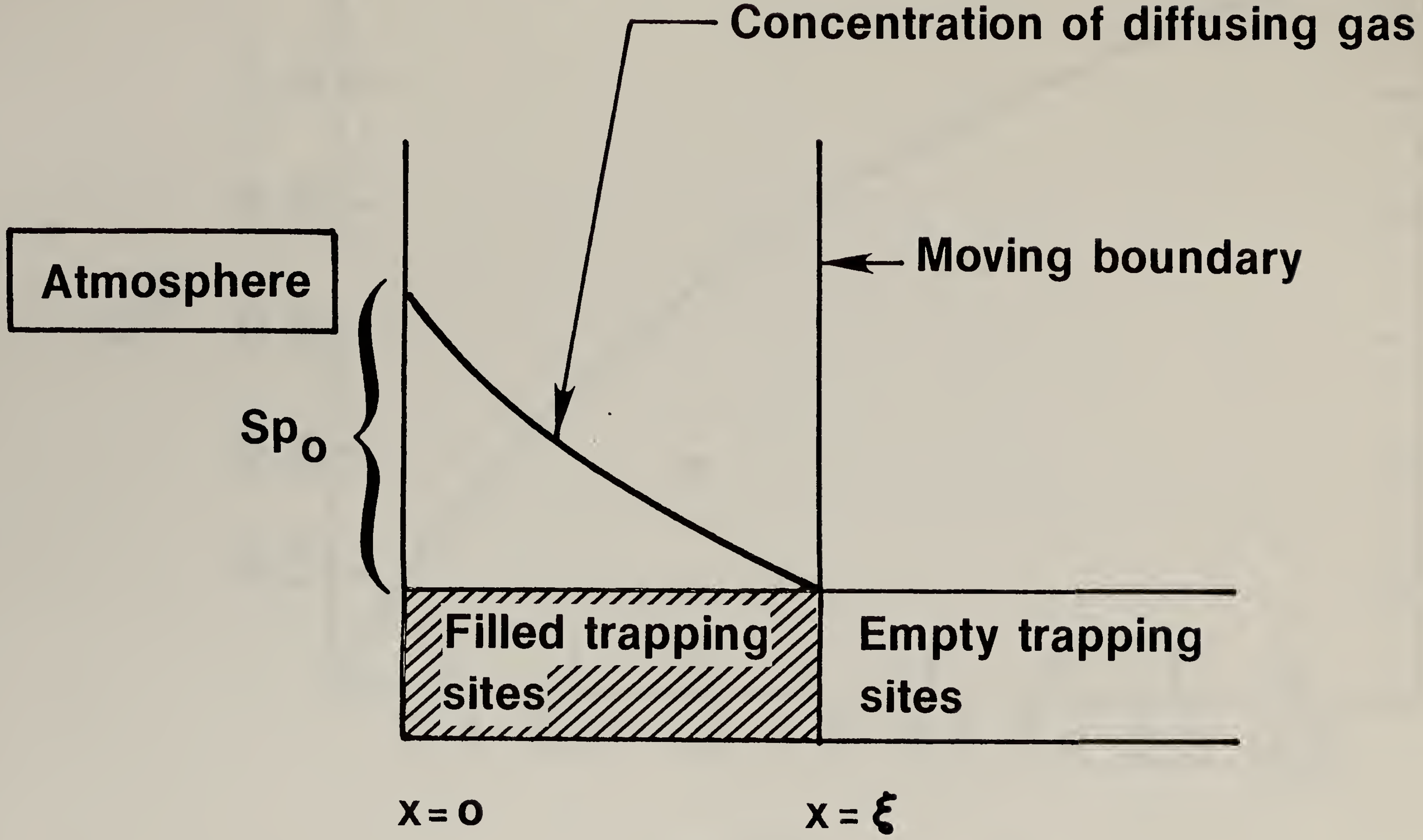

Concentration of diffusing gas
Moving boundary
Atmosphere
Sp_o
Filled trapping sites
Empty trapping sites
x = 0
x = ξ

FIGURE 3

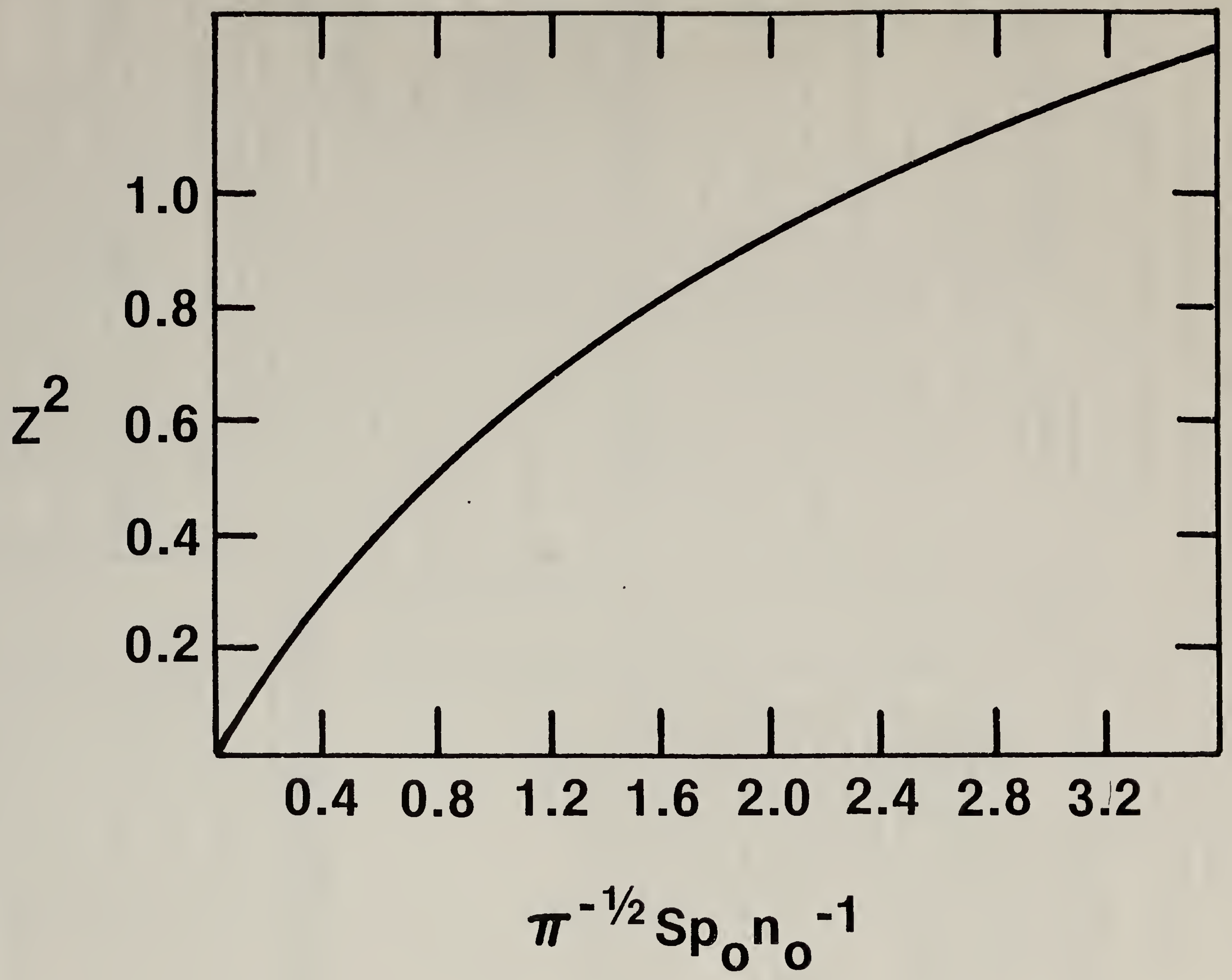
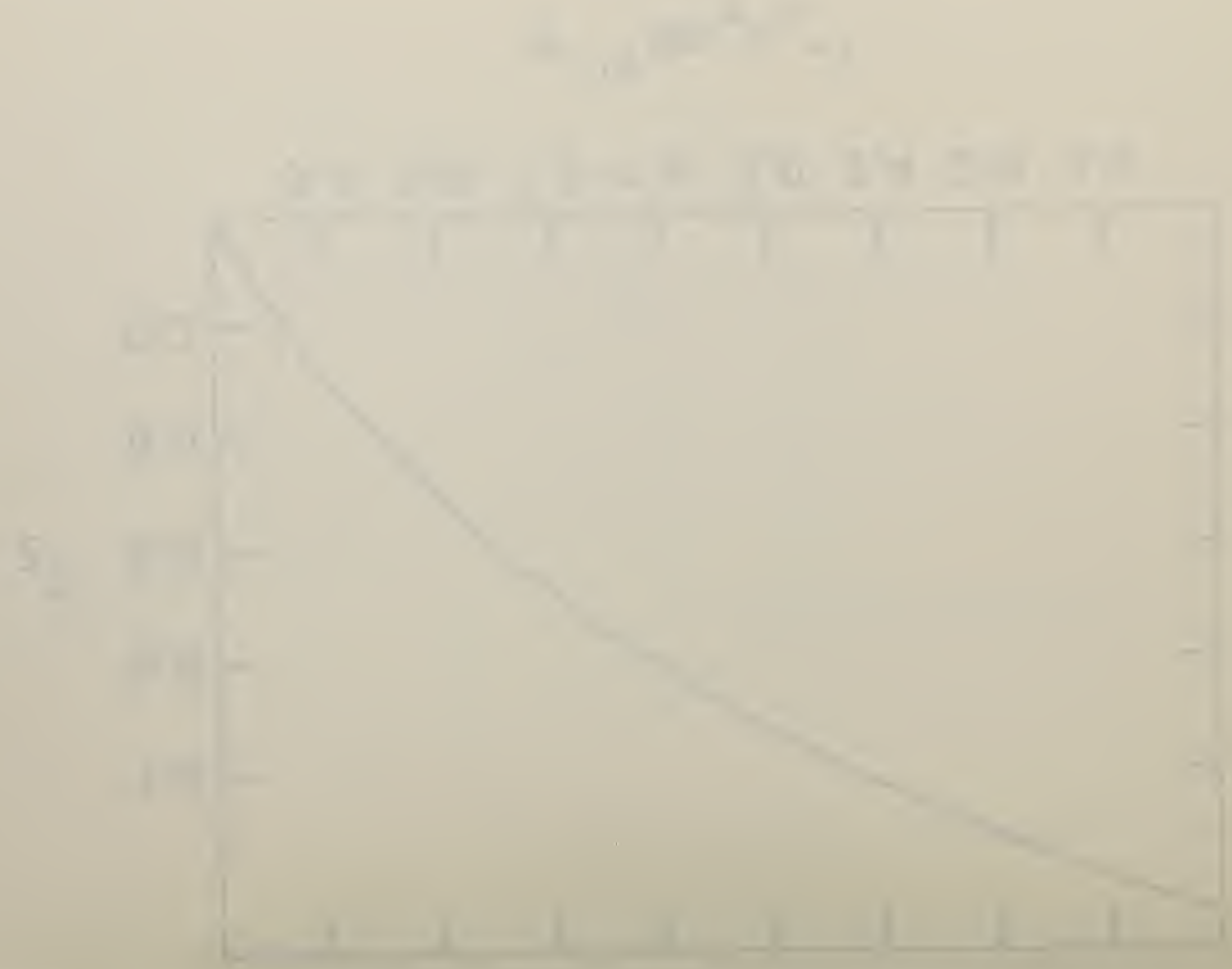


FIGURE 4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☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Two mathematical models of a personal monitoring device are analyzed. The purpose of the device, which is to be worn by an individual, is to indicate the level of exposure to various criteria air pollutants such as O_3, SO_2, NO_2, CO during the time period which might range from 24 hours to a week or longer. The goal of the analysis of the models is to determine how the quantity of pollutant which is collected is related to the average pollutant concentration and how material constants such as solubility and diffusion coefficients affect the operation of the device.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

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