By William K. Fowler

Fundamentals of passive vapor sampling

PASSIVE vapor-sampling devices are gaining wide acceptance among industrial hygienists in settings where exposures of personnel to potentially hazardous vapors must be measured. In contrast to an "active" sampler, in which the air sample is brought into contact with a detector or collector device by forced convection or pumping, the passive sampler typically collects the species of interest (i.e., the analyte) from its immediate surroundings by virtue of the natural diffusion[1] (or permeation[2]) of the species into the sampler and from there into or onto a trapping medium or "sink." The amount of analyte thus collected is related to the integrated dose or time-average concentration of the analyte in the sampled environment. Relative to active sampling systems, passive samplers are generally simple in construction and require no power for operation. Moreover, they are small and light in weight, are easy to prepare and use, and are often low in cost.[3]

Diffusion and permeation samplers

A diffusion sampler typically consists of a tube, a parallel cluster or matrix of tubes, or an item of hardware providing tube-like pores or channels with an absorbent, adsorbent, or reactive material located at one end of the diffusion zone formed by the tubes, pores, or channels. The other end of the diffusion zone is generally open to the atmosphere. A diagram of a simple tube-type diffusion sampler is shown in *Figure 1*.

A permeation sampler differs from a diffusion sampler primarily in that the rate-limiting analyte concentration gradient (i.e., the resistance to mass transport) occurs within a permeable membrane or other permeation barrier positioned between the atmosphere being sampled and a "sink" or trapping medium as described for the diffusion sampler. Thus, one face of the membrane is in contact with the air, and the other face is in contact with the trapping medium, so that the entire diffusion or permeation zone lies within the membrane. In a few designs, however, there is a layer of air between the inner face of the membrane and the trapping medium; this air layer constitutes an additive diffusional resistance in series with the permeation resistance provided by the membrane. A typical permeation sampler is shown in *Figure 2*.

Fick's first law of diffusion

The rate of diffusion of analyte molecules from the open air at the sampler inlet to the "sink" or analyte-trapping material at the other end of the diffusion zone is governed by Fick's first law of diffusion:[4]

$$U = -DA\,\frac{dc}{dx} \qquad (1)$$

where U is the diffusive transport rate (mol/sec), D is the analyte diffusivity (i.e., diffusion coefficient) in air (cm^2/sec), A is the diffusion path cross-sectional area (cm^2), x is the distance along the diffusion path (cm), and c is the analyte concentration at point x (mol/cm^3). This equation may be integrated over the length, L, of the diffusion path to yield a useful expression for the analyte sampling rate. Under normal operating conditions, it may be as-

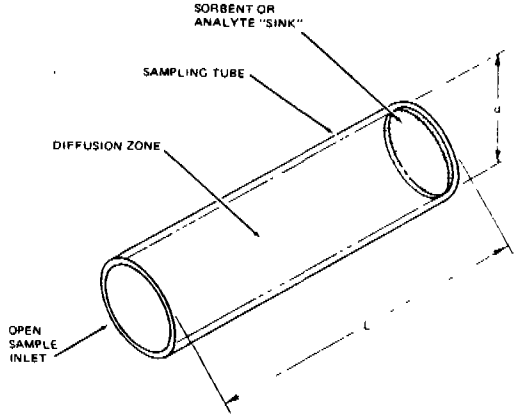

Figure 1 *A simple tube-type diffusion sampler*

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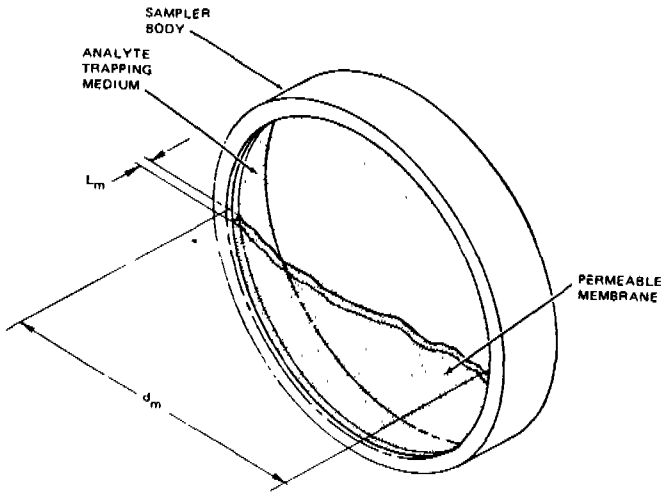

Figure 2 *A typical membrane-type permeation sampler.*

sumed that the concentration of analyte vapor at the surface of the trapping material is zero and that analyte concentration at the sampler inlet is equal to the ambient concentration, C_a. With these assumptions, the result of the integration of Eq. (1) is as follows:

$$U = \frac{DAC_a}{L} \tag{2}$$

Within a given exposure time, t (in seconds), the amount, M (in mol), of analyte collected by the sampler is as follows:

$$M = Ut = \frac{DAC_a t}{L} \tag{3}$$

Note that the "effective" volume sampling rate (Z, in cm³/sec) is given by DA/L.[5] Hence, if Z for a given sampler is, for instance, 2 cm³/sec, then that sampler will accumulate during a 1-sec interval the amount of analyte that is present in 2 cm³ of the ambient atmosphere, exactly as would a conventional pump-operated sampling tube sampling at the same rate.

Note also that Eq. (2) resembles Ohm's law, $I = E/R$, where I is the current, E is the electromotive potential, and R is the resistance.[6] Specifically, U in Eq. (2) is analogous to current; DC_a to electromotive potential; and L/A to resistance. Because electrical resistances in series are additive, diffusional resistances (L/A) connected in series between the ambient atmosphere and the analyte-trapping medium should also be additive. This was found experimentally to be the case.[6]

Frequently in instances where two or more series-linked diffusional resistances occur in a sampler, the resistor nearest the sample inlet is a microporous membrane or other similar covering that serves as a "windscreen." The windscreen prevents the inner diffusion gradient from being disrupted by air movement in the vicinity of the inlet. As long as the pores or channels in the windscreen are greater than about 1 μm in diameter,[1] the windscreen's effect upon the diffusion characteristics of the sampler can be determined straightforwardly with Eq. (1).[7,8] Frequently, the windscreen's contribution is negligible.

Like gaseous diffusion, diffusion within a permeable membrane (i.e., permeation) is also governed by Fick's first law, and therefore the above-described relationships also hold for membrane permeation samplers. For many such devices, however, the diffusion zone is wholly confined to the interior of the membrane; therefore, U in the above equations is the diffusive transport rate through the membrane (U_m), D is the diffusion coefficient of the analyte species within the membrane (D_m), and C_a should be replaced with another symbol (say, C_m) that represents the analyte concentration in the membrane at its outer surface. Moreover, the dimensions A, X, and L are physical dimensions of the membrane. (Let A_m and L_m be the area and thickness of the membrane, respectively.) To obtain membrane-specific versions of Eqs. (2) and (3) in this manner [i.e., by integration of Eq. (1) over the membrane thickness], one must assume that the analyte concentration at the inner membrane surface is zero and that the analyte concentration in the air immediately adjacent to the outer membrane surface is the same as the ambient analyte concentration. These assumptions are probably at least approximately valid for most membrane permeation samplers and for most real sampling situations.

Note that Fick's first law by itself does not suffice to relate the ambient analyte vapor concentration (C_a) to any measurable parameter associated with the permeation sampler. According to Henry's law, however, the analyte concentration in the membrane is directly proportional to the analyte concentration in the air adjacent to the membrane:

$$C_m = QC_a \tag{4}$$

where Q is a proportionality constant that contains Henry's law constant. Clearly, therefore, Eq. (4) can be substituted into the membrane-specific versions of Eqs. (2) and (3) to obtain the needed relationships. Eq. (3), for example, then becomes:

$$M = U_m t = \frac{QP_m A_m C_a t}{L_m} \tag{5}$$

At least one group of researchers chose to define the product QD_m as the membrane permeability,[8] but most researchers in the field of permeation sampling have found it convenient to lump all of the constant terms into a single "permeation constant," K,[9–11] and hence Eq. (5) may be rearranged to give:

$$K = \frac{L_m}{QD_m A_m} = \frac{C_a t}{M} \tag{6}$$

In practice, K is usually determined for a permeation sampler by measuring M after exposure of the sampler for time t to standard test atmospheres containing known concentrations of the analyte. Because large variations in membrane thickness (L_m) from one sampler to the next are common,[9,12] K must be determined individually for each sampler. Experiments with a variety of membranes have disclosed that many membrane materials exhibit a permeation constant that varies with the analyte concentration.[13] This is a highly undesirable characteristic for a permeation sampler. Fortunately, however, this has not been a major problem with membranes fabricated from polydimethyl siloxane (dimethyl silicone).

Determination of diffusivity, D

The diffusivity of a molecular species in air is a function of certain intrinsic properties of the species and may be measured experimentally[5] or may be calculated from any of a variety of empirical and semiempirical equations. In a study of nine such equations,[14] it was concluded that the equation of Hirschfelder, Bird, and Spotz agreed most closely with experimental values of D for high-molecular-weight compounds, whereas the Chen and Othmer equation or the Wilke and Lee equation provided more accurate values for low-molecular-weight vapors. In this study, however, many of the calculated results were not within ±5% of the observed values, which suggests that the determination of D may be a significant source of error in passive diffusional sampling. A typical value of D for an environmental pollutant (such as dichloroethylene) is about 0.1 cm²/sec,[15] but values of D for different species vary too widely for an "average" value to suffice in Eq. (1) for all organic pollutants.[1]

Effect of environmental factors

The most significant environmental factors likely to affect the performance of a diffusion-type sampler are the temperature, pressure, and humidity of the atmosphere. Changes in temperature and pressure result in changes in the analyte diffusivity according to the following equation:

$$D = \frac{K' T^n}{P} \tag{7}$$

where T is ambient temperature, P is atmospheric pressure, K' is a proportionality constant, and n is a number that kinetic theory predicts to be 1.5,[16] but that may actually be as high as 2.1.[1,16] To appreciate the magnitude of the dependency of D upon T and P, note that an increase in T from 5° to 35°C causes a 16% increase in D even when n is only 1.5, and an increase in P from 28 to 32 in. Hg causes a 14% decrease in D.[4]

The rate at which a diffusion sampler collects the analyte species, as given by Eq. (2), does not depend on T and P in the manner given for D in Eq. (7). This is because C_a, which appears in Eq. (2) along with D, also depends on T and P. Changes in T and P produce changes in the volume occupied by a given mass of atmosphere according to the ideal gas laws, and therefore, the atmospheric concentration of an analyte species (C_a), expressed as a mass per unit volume, must vary in direct proportion to P and in inverse proportion to T:

$$C_a = \frac{K'' P}{T} \tag{8}$$

If Eqs. (7) and (8) are substituted into Eq. (2), it will be seen that the sampling rate U [and M in Eq. (3)] is directly proportional to T^{n-1} and is completely independent of P.

It is appropriate to examine the effect of T and P on the analyte concentration that might be calculated from Eq. (3) after measurement of M, the total amount of analyte collected. First, it is convenient to rearrange Eq. (3) as follows:

$$C_a = \frac{ML}{DAt} \tag{9}$$

Now, let us assume that D for the analyte is accurate at $T = T_1$ and at $P = P_1$ (i.e., $D = D_1$) and that a sampling experiment is conducted at $T = T_2$ and $P = P_2$. The calculated value of C_a is given by Eq. (7) as follows:

$$C_a \text{ (calc)} = \frac{ML}{D_1 AT} \tag{10}$$

The true value of C_a could be computed, however, if the value of D were known accurately at T_2 and P_2 (i.e., if $D = D_2$):

$$C_a \text{ (true)} = \frac{ML}{D_2 At} \tag{11}$$

Thus, the ratio C_a (calculated)/C_a (true) = D_2/D_1, and after incorporation of Eq. (7), this expression becomes:

$$\frac{C_a \text{ (calc)}}{C_a \text{ (true)}} = \frac{D_2}{D_1} = \frac{P_1}{P_2}\left(\frac{T_2}{T_1}\right)^n \tag{12}$$

Clearly, therefore, both temperature and pressure fluctuations can lead to an error in the calculated analyte concentration.

A number of researchers apparently feel, however, that it is appropriate to correct all measured ambient pollutant concentrations to the equivalent concentrations at some standard temperature and pressure by use of the ideal gas laws.[4,5,17] This procedure was recommended by the National Institute for Occupational Safety and Health (NIOSH) and was incorporated into the regulations of the Occupational Safety and Health Administration (OSHA).[18] According to this procedure:

$$C_a \text{ (corrected)} = C_a \text{ (true)} \cdot \frac{T_2}{T_{std}} \cdot \frac{P_{std}}{P_2} \qquad (13)$$

where T_{std} and P_{std} refer to the chosen standard temperature and standard pressure, respectively, and T_2 and P_2 are as defined previously. If T_1 in Eq. (12) is chosen to be T_{std} and P_1 is chosen to be P_{std}, then Eqs. (12) and (13) can be combined as follows:

$$\frac{C_a \text{ (calc)}}{C_a \text{ (corrected)}} = \left(\frac{T_2}{T_{std}}\right)^{n-1} \qquad (14)$$

Hence, if D is accurately known at the standard temperature and pressure, then the analyte concentration measured by a diffusion sampler at any given temperature or pressure will differ from the corrected true concentration only in proportion to T^{n-1}. (There is no dependence upon P at all.) For this reason, researchers often state simply that diffusion sampler error is a function only of $T^{1/2}$, where it is assumed that $n = 1.5$ (i.e., $n - 1 = 1/2$), even though the error is actually a function of T^n/P as given by Eqs. (7) and (12). The situation is further complicated by the frequent use of the concentration unit, parts per million, because vapor concentrations given in this unit are independent of atmospheric temperature and pressure. When this unit is used, diffusion sampler error is always a function of T^{n-1} and is independent of P. This circumstance seems to have led to ambiguity and consequent misunderstanding among workers in the field of industrial hygiene dosimetry.[17,19]

With regard to the effect of humidity upon diffusion sampler performance, humidity has essentially no effect upon the diffusion parameters of Eq. (2), provided that the sampled atmosphere does not contain enough water vapor to cause an appreciable

change in the mean molecular weight of air. This is a valid assumption in most industrial hygiene applications. However, humidity can substantially diminish the saturation capacity of the analyte-trapping medium, especially if the trapping medium is a solid sorbent material.

Although membrane permeabilities are, in general, drastically affected by temperature,[13] this does not seem to hold true for membranes prepared from polydimethyl siloxane. For example, no significant temperature effects were observed among silicone membrane samplers designed for the determination of hydrogen sulfide,[11] chlorine,[20] or vinyl chloride.[5,21] Although rather substantial temperature effects were noted among samplers of this type that were intended for use in the sampling of carbon monoxide[22] and sulfur dioxide,[13,23] these effects were nevertheless small in relation to those observed among other types of membranes. This apparently unique property of silicone membranes has been explained in terms of the very small activation energy of permeation for many substances in silicone rubber.[8]

The effects of atmospheric pressure and of humidity upon the performance of a membrane permeation sampler are probably not significant.[13]

Sampler response time

Considerably different concentration readings for workplace pollutants have resulted from samplers positioned only a few feet apart on a worker's body.[12] Obviously, therefore, a sampler may be exposed to quite sudden changes in analyte concentration at any point during a given sampling interval, provided that the sampler or the air around the sampler is moving. Thus, it is important that the sampler be able to respond rapidly to a change in analyte concentration.

The response time of a diffusion sampler is the time required for the sampling rate, U [Eq. (2)], to adjust completely or nearly completely to a sudden change in analyte concentration in the atmosphere. A simple and convenient measure of response time is the average residence time of the analyte within the diffusion zone of the sampler.[4,5,18] If a linear concentration gradient is assumed in a tube-type diffusion sampler (see Figure 1) such that $c = C_a$ at the tube inlet and $c = 0$ at the surface of the trapping medium, the average concentration of analyte in the diffusion zone is $C_a/2$. Moreover, the volume of the diffusion zone is equal to the volume of the tube, $A \cdot L$, where these terms are as defined for Eq. (2). Note that the amount, M, of analyte to be found within the diffusion zone is given by:

$$M = \frac{C_a A L}{2} \quad (15)$$

If this value is substituted for M in Eq. (3) and the equation is solved for t, the result is the residence time of the analyte in the diffusion zone of the sampler:

$$t_r = \frac{L^2}{2D} \quad (16)$$

Other authors have employed slightly different versions of this relation.[8]

Derivations of Eq. (16) from Fick's second law of diffusion have been published showing that at time $t = t_r$, the diffusive transport rate, U, has undergone approximately 63% of the full change that it will ultimately undergo in response to a step change in analyte concentration.[1] The rate of change of U decreases exponentially with time, so that a time interval equal to several times t_r is required for the occurrence of a change in U that is equal or very nearly equal to the full anticipated change.

Equation (16) predicts that the response time of a diffusion sampler for a given analyte of fixed diffusivity should depend only on the square of the length of the diffusion pathway. If a microporous membrane (whose pores may be only 0.0025 cm long) is employed in the diffusion path, the response time should be extremely fast unless the diffusivity of the analyte suffers as a result of the small dimensions of the pores.[1,8] Typically for diffusion samplers, however, the response time varies from about 0.5 sec[5] to several minutes.[16,17]

Although it is possible to calculate the response time of a membrane sampler,[8] accurate values for the necessary parameters are not generally available, and therefore response times are usually measured experimentally in the laboratory. For silicone membranes, response times of less than 1 min have been achieved for a number of different analytes[9,11,20] and have been found to be on the order of a few minutes for certain other analytes.[13,23] These response times are probably satisfactory for most applications of passive samplers.

Effect of air face velocity

The velocity of the air around the passive sampler can affect its rate of analyte uptake. The diffusivity itself is independent of air movement, and thus the adverse effect of moving air arises only from its ability to alter the length (i.e., the diffusional resistance) of the diffusion pathway. Generally, it is the increase in length of the diffusion pathway caused by stagnant air conditions that leads to an error in sampling.[7,24] This problem results from the depletion of the analyte species in the air immediately external to the sampler inlet. Note that this extension of the sampler diffusion gradient causes an effective increase in the L term of Eq. (2), thereby decreasing the diffusive transport rate, U.[25] Hence, air stagnation invariably leads to erroneously low results.

It can be shown from mass transfer theory that the diffusive resistance experienced by a passive sampler due to an external analyte concentration gradient is inversely proportional to $V^{0.4}$, where V is the face velocity of ambient air relative to the sampler inlet.[4] This relationship suggests that the external diffusive resistance should diminish rapidly with relatively small increments of V above zero until a velocity level is reached beyond which the sampler performance quickly becomes virtually insensitive to velocity. This critical minimum velocity has been observed and reported by various researchers for their respective samplers, and it is usually about 15 ft/min.[4,7,25] For dosimeters worn by workers in industrial atmospheres, however, face velocities this low are rarely experienced.[4,7]

In addition to the problem due to low face velocities, the opposite problem also may be encountered due to very high face velocities. This problem arises from a disturbance of the sampler internal diffusion gradient near the sampler inlet so that the gradient is effectively shortened and the diffusion rate is increased. This problem is especially severe for the single, open-tube-type samplers and is most severe when the wind impinges upon the sampler inlet at a 120° to 135° angle with the sampler tube.[1,17]

Air velocity effects of both types may be minimized by maximizing the length of the sampler internal diffusion pathway.[25,26] However, lengthening the diffusion pathway also increases the sampler response time [Eq. (16)] and decreases the diffusive transport rate [Eq. (2)]. Moreover, in the design of a passive sampler, care frequently must be taken to limit the diffusive transport rate so that the sampler's analyte-trapping medium is not saturated when working at the upper end of the ranges of analyte concentrations and sampling times. Hence, this factor must also be taken into account when optimizing the length of the diffusion pathway. Interestingly, a diffusion pathway that is from 3 to 8 times longer than it is wide has proven to be optimal for a considerable variety of passive diffusion samplers.[5,16,17,24,25]

In principle at least, membrane-permeation samplers are subject to the same adverse effects of stagnant air as described previously for diffusion sam-

plers. However, the cross-sectional area of a permeation sampler "inlet" (i.e., membrane surface area) is often far larger than the inlet cross-section for a diffusion sampler. Accordingly, a permeation sampler collecting analyte species at the same absolute rate (mol/sec) as a diffusion sampler may not display nearly as great a tendency to deplete the air of analyte as does a diffusion device. Thus, the permeation sampler may not be as likely as the diffusion sampler to produce an external analyte concentration gradient, and in practice, air stagnation has not been a problem for the permeation sampler.[12,21,27]

Because air movement cannot affect the analyte concentration gradient within or behind the membrane, the internal gradient-disruption effect of high wind velocities described above in connection with diffusion samplers cannot occur in permeation samplers.

Diffusion versus permeation sampling

Both the diffusion sampling technique and the permeation sampling technique offer a unique set of advantages and limitations for environmental sampling. Generally, diffusion samplers are amenable to thermal desorption into a gas chromatograph;[24,25,28] they can be mass produced cheaply enough for one-time, throw-away use;[2] and they do not require calibration.[2] However, they may be subject to errors caused by variations in air face velocity and also by fluctuations in temperature. Moreover, the trapping media that are suitable for use in diffusion samplers are confined primarily to adsorptive or reactive solids (as opposed to liquids, which are useful in permeation devices). These solids, in turn, are more susceptible than liquids to the deleterious effects of atmospheric humidity.[12]

Permeation samplers, on the other hand, are virtually free from humidity effects (especially when a liquid analyte-trapping medium is employed); they can make use of almost any analyte-trapping medium (liquid or solid); they are not especially susceptible to errors caused either by variations in wind velocity or, if a silicone membrane is used, by variations in temperature; and they generally can be used repeatedly.[2] However, permeation samplers also tend to be costly, and they typically require calibration.[2] Even when calibrated, permeation samplers may exhibit a variable working concentration range (and variable detection limits) because of the variation in membrane permeabilities from one sampler to the next.[20]

The field of passive sampling technology is currently in a state of rapid development, and passive samplers of both the diffusion and permeation types are continuing to appear frequently in the marketplace.

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