Ann. occup. Hyg., Vol. 32, No. 3, pp. 333–343, 1988.
Printed in Great Britain.

0003–4878/88 $3.00 + 0.00
Pergamon Press plc
British Occupational Hygiene Society.

PERFORMANCE OF THICK-SORBENT DIFFUSIVE SAMPLERS

DAVID L. BARTLEY, MARY LYNN WOEBKENBERG and JUDD C. POSNER
Division of Physical Sciences and Engineering, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226, U.S.A.

(*Received* 4 *June* 1987 *and in final form* 26 *November* 1987)

Abstract—Errors of estimates of concentration in the diffusive sampling of analytes weakly bound to finite-thickness sorbents are investigated both theoretically and experimentally. Experimental data are presented for sampling concentration pulses of trichloroethylene, using a column of activated charcoal as sorbent. Analysis indicates that analyte loss results in errors in estimates of 8-h time-weighted averages (TWA) between −17 and 51%, the extreme values corresponding to short pulses occurring at the beginning or end of the sampling period, respectively. Experiments were also conducted on pulse sampling using a sampler which employs a liquid (in this case, water) column as sorbent. Both acetone (weakly bound) and methanol (more strongly bound) were studied so as to cover a range of physical phenomena. Limits of several mathematical approximations are discussed within the framework of these experiments.

INTRODUCTION

SEVERAL recent papers have described possible sampling errors in estimating time-weighted averages (TWA) of time-dependent concentrations using diffusive monitors. The error is a consequence of analyte loss from some diffusive samplers back into the atmosphere during the course of sampling. Depending on the specific sampler configuration, such losses may occur either directly from the sampler air spaces (HEARL and MANNING, 1980; UNDERHILL, 1983; BARTLEY *et al.*, 1983), or from the sampler walls or the sorbent itself (POSNER, 1981; FEIGLEY and CHASTAIN, 1982; GREGORY and ELIA, 1983; BARTLEY, 1983; COUTANT *et al.*, 1985; BERTONI *et al.*, 1985; POSNER and MOORE, 1985).

Alternatively, the analyte-loss error is related to a constantly decreasing sampling rate, where concentrations are constant with time. In the case of thick-sorbent samplers, such a decrease corresponds to the gradual consumption of sorbent. As the diffusion length increases, the sampling rate falls off.

Note, however, that in the absence of analyte loss a variable sampling rate does not necessarily imply problems with estimation accuracy. If the sorbent (distributed along the sampling direction) binds the analyte tightly, then it is possible to show (BARTLEY, 1986) that a (non-linear) sampler calibration can give accurate estimates of the time-weighted average concentration in terms of the amount of sorbed analyte, even if sorbent is consumed. Time-dependence of the concentration poses no problem. This is, in fact, the rationale behind the performance of colour-change monitors (Mine Safety Appliances Co.; GONZALEZ and SEFTON, 1983) and also of an extended-sorbent nitrous oxide sampler manufactured by Perkin–Elmer (COX and BROWN, 1984).

Our paper deals with analyte less tightly bound to a sorbent of significant thickness such as in the sampling of some analytes by the ORSA 5 sampler (National Draeger Inc.) or by a similar sampler manufactured by Perkin–Elmer (BROWN *et al.*, 1981). In

this case, analyte may diffuse slowly through unsaturated sorbent. If the diffusion rate is slow, long time periods may be required for transients (from external concentration variations) to disappear. As in the case of transients in the sampler air spaces, errors can thereby be introduced into the exposure estimate. Here, however, since the relaxation times for the transient decay may be of the order of the sampling period duration, the errors may be significant even in sampling over long sampling periods (e.g. 8 h).

We describe an experiment giving the ORSA 5 sampler response to trichloroethylene concentration pulses within an 8-h time period. The data are analysed in terms of a model which predicts extreme values of the errors expected in estimating time dependent concentrations. Results of a similar experiment using a liquid-sorbent sampler (GMD Systems Inc., Hendersonville, Pennsylvania, Cat. No. 540-03) in measuring both acetone and methanol concentrations are also presented. The data are found to represent separate limiting approximations of the mathematical model described.

THEORETICAL

The highlights and major results of the theory behind the extended sorbent diffusive sampler are presented here, while details of the calculations are relegated to the Appendix. Analysis is developed within the framework of a sorbent characterized by a diffusion constant D' (generally small in comparison with diffusion rates D of gases in air). Furthermore, we assume equilibrium proportionality (Henry's law) at the interface between concentrations C in air and ρ in the sorbent column:

$$\rho = HC, \tag{1}$$

where H is Henry's law constant. Equation (1) is valid for liquid sorbents or for solid sorbents in the limit of weak sorption. More specifically, in the case of solid sorbents, the generally singular non-linear (Dubinin or Freundlich) isotherm is approximated only over a very limited range of concentrations in the linear form given in Equation (1). The more general non-linear theory is considerably more difficult and must be approached using mathematical tools other than those used here. We further assume that the in-sorbent diffusion rate D' or thickness L of the front membrane or air space is small enough to ensure that the corresponding transient decay times are much shorter than those in the sorbent itself.

These assumptions result in estimates of the mass $m(t_s)$ accrued during sampling period t_s in terms of the time-dependent external concentration $C_{ext}(t)$ at time t:

$$m(t_s) = (DA/L) \int_0^{t_s} dt' g(t_s - t') C_{ext}(t'), \tag{2}$$

where $g(t_s - t')$ is a response function which characterizes the sampler and which we calculate in three useful situations:

General case

In the general case of finite sorbent thickness d, calculation described in the Appendix leads to an expression for the sampler response function $g(t)$ given by

$$g(t) = \sum_j \exp[-(k_j)^2 D' t] \sin(2k_j d)/[k_j d + 0.5 \sin(2k_j d)], \tag{3a}$$

where k_j is a solution of the transcendental equation:

$$\tan(k_j d) = (d/l)/[k_j d] \tag{3b}$$

and where the constant l is defined by

$$l = LHD'/D. \tag{3c}$$

Although Equation (3) is quite complicated, calculation by computer is straightforward. Furthermore, if transients in the sorbent are long-lived relative to the sampling period, then a much simpler expression may be derived by approximating the sorbent as an infinite slab (described in the next section).

Infinite sorbent

Often diffusion within the sorbent is so slow that only a part of the sorbent near the sampler entrance is exposed significantly to analyte during the sampling period. In this case the sorbent may be approximated as infinitely thick, i.e. with $d = \infty$. The sampler response function g then simplifies to (see Appendix)

$$g(t) = \exp[\beta t]\ \mathrm{erfc}[(\beta t)^{1/2}], \tag{4a}$$

where β is defined as

$$\beta = D'/l^2 \tag{4b}$$

and where erfc is the error function complement (Abramowitz and Stegun, 1964). Therefore, the time-dependence of the mass m remaining at time t after a single concentration pulse as in experiments described in the text is

$$m = m(0)\ \exp(\beta t)\ \mathrm{erfc}[(\beta t)^{1/2}]. \tag{5}$$

Because of its simplicity, Equation (4) should be used rather than Equation (3) whenever transients are long-lived over time scales of interest. For example, Equation (3) provided no improvement over Equation (4) in modelling either GMD badge acetone sampling or Draeger ORSA 5 trichloroethylene sampling described below.

Exponential desorption

An important limiting case of Equation (3) is obtained when transients within the sorbent die out quickly. This occurs when binding to the sorbent is strong enough and diffusion is sufficiently rapid. In this case, the analyte is held long enough and the sorbent mixed by diffusion rapidly enough for the concentration in the sorbent to be nearly always constant spatially.

The concentration $C(0)$ just outside the sorbent is then simply related to the total sorbed mass m within sorbent volume V $(= dA)$ by Henry's law:

$$C(0) = m/(VH). \tag{6}$$

Fick's law giving the sampling rate through an air space of length L,

$$\mathrm{d}m/\mathrm{d}t = [DA/L]\ [C_{\mathrm{ext}} - C(0)], \tag{7}$$

can therefore be rewritten as

$$\mathrm{d}m/\mathrm{d}t + m/\tau = [DA/L]C_{\mathrm{ext}}, \tag{8}$$

where the loss time τ is given by

$$\tau = VH/[DA/L]. \tag{9}$$

Equation (8) is solved, given arbitrary time variation in the external concentration C_{ext}, by a response function $g(t)$:

$$g(t) = \exp(-t/\tau) \tag{10}$$

[even simpler than Equation (4)] for use in Equation (2).

As a specific example, consider the loss of analyte from initial mass $m(0)$ when exposed to clean air for time t. Either application of Equation (2), or else direct solution of Equation (8) gives:

$$m = m(0) \exp(-t/\tau). \tag{11}$$

Expressions as in Equation (11) are very simple and are accurate providing the time τ_{trans} required for transients to die out is short compared with the loss time τ:

$$\tau_{trans} \ll \tau. \tag{12}$$

The time τ_{trans} is given (BARTLEY *et al.*, 1983) by

$$\tau_{trans} = \pi^{-2} d^2/D'. \tag{13}$$

Therefore, Equation (12) can be expressed [using Equations (9) and (13)] as

$$(d/L)(D/D')H^{-1}\pi^{-2} \ll 1. \tag{14}$$

Equation (14) can be applied, for example, in the specific case of the GMD badge sampling of methanol described below. In this case $H = 5280$ (HINE and MOOKERJEE, 1975), $d \sim L$, $D \sim 0.1$ cm^2 s^{-1} (the diffusion rate in air), $D' \sim 10^{-5}$ cm^2 s^{-1}. Therefore, the left-hand side of Equation (14) is ~ 0.2, which (being $\ll 1$) explains the success of the simple exponential model [Equation (10)] in modelling the data presented below.

EXPERIMENTAL

Two sets of experiments were conducted using thick-sorbent samplers for measuring time-varying concentrations. One set involved the use of activated charcoal spread out over a length of about 2 cm in a Draeger ORSA 5 tubular sampler. The other experiment used a GMD liquid-sorbent sampler with liquid depth about 1 cm.

Activated charcoal

The purpose of the first set of experiments was to compare TWA concentration estimates in sampling concentration spikes occurring at different times during a lengthy sampling period. The Draeger ORSA 5 sampler and dimensions are depicted in Fig. 1. The sampler consists of a glass tube containing a bed of activated charcoal held by fibrous plugs at each end. Both ends of the tube are kept capped when not in use. During a sampling period, both caps are removed so that analyte is sampled into both ends.

Twelve capped ORSA 5 samplers were placed in a sealed exposure chamber (20°C, 50% relative humidity) containing 25 ppm trichloroethylene [selected because of

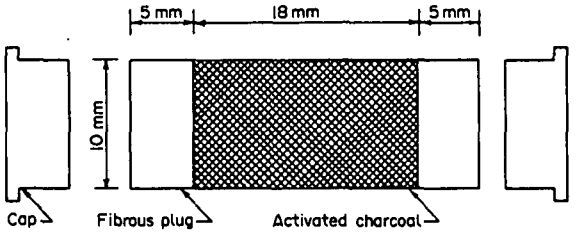

FIG. 1. Dimensions of Draeger ORSA 5 diffusive sampler.

suspected weak binding to activated charcoal and yet listed (National Draeger Inc.) as a candidate analyte in the ORSA 5 instruction manual]. Ten samplers inside the exposure chamber were uncapped at $t = 0$ min, and the two additional samplers remained capped as controls. At $t = 5$ min all samplers were removed from the chamber and placed in normally convecting trichloroethylene-free air. Throughout the day, the 10 samplers were re-capped individually, one at $t = 15$, 30 and 45 min, and at each hour for 7 h (25 200 s).

The rationale behind this experimental design is that if a sampler loses analyte continuously following exposure, then the TWA estimates from samplers exposed to pulses early in a sampling period would be low compared with TWA estimates from samplers exposed to pulses later in a sampling period. Since the *true* TWA values of the pulse are identical (i.e. pulse heights and duration are identical), any variation in TWA estimates is due simply to differences in the time intervals over which the samplers lose material. This experiment should, therefore, detect a potential error associated with samplers which lose analyte. In fact, since an arbitrary time-dependent concentration can (within resolution limits set by the pulse duration) be built up by superimposing many pulses, this type of experiment can detect the maximum bias in the estimation of TWA averages if the sampling rate time-dependence is dominated by analyte loss (BARTLEY *et al.*, 1987).

The shifting of concentration pulses reproducibly within an 8-h sampling period is quite difficult. Therefore, in this experiment only a single pulse was used, and the sampling period was shifted instead. In this way, identical exposure of the samplers is ensured, even if the true TWA concentration is uncertain.

The data from this experiment are presented in Fig. 2. The samplers used as controls were found free of analyte. Also shown is a numerical fit (solid curve) to the data points using the theoretical model of Equation (5). The use of such a model permits calculation of the single-sample random error or the coefficient of variation (CV) which, as indicated in the figure, was equal to about 6%. The model also gives an estimate of the sampled mass expected if the concentration were constant over the entire sampling period instead of being pulsed. This value is shown as the dashed line in Fig. 2.

Although the (6%) random error appears to be under control, deviation of the collected masses from the dashed line indicates excessive bias associated with analyte loss. As seen from Fig. 2, the largest bias occurs at $t = 0$ (allowing little loss time) following the pulse and may be calculated to equal 51% relative to the dashed curve. The minimum bias occurs at $t = 8$ h (28 800 s) following the pulse and is found to equal -17%. [Note that this *negative* bias results from sampler calibration using a constant

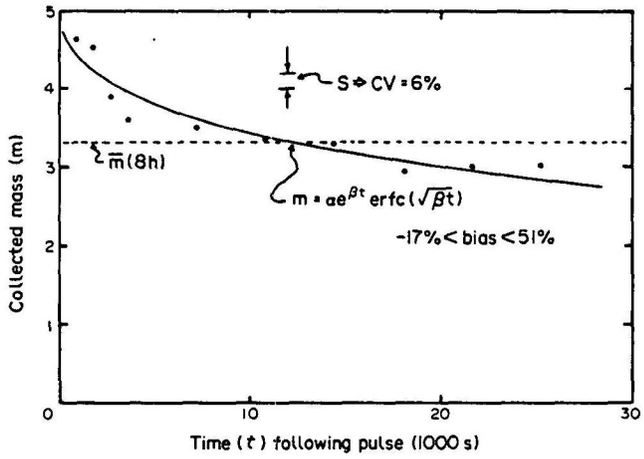

FIG. 2. Measured mass (μg) remaining in open sampler after a time (*t*) following a single pulsed concentration of trichloroethylene. Solid curve represents a best fit to data using model described in text.

concentration over the entire sampling period (8 h), rather than using the initial instantaneous sampling rate, for example. Such use of an *apparent* (rather than instantaneous) sampling rate permits unbiased estimates of fluctuating concentrations by averaging over many sampling periods.] Such large biases do not meet the NIOSH Standards Completion Programme (GUNDERSON and ANDERSON, 1980) (SCP) requirement of less than 25% single-sample overall error at the 95% confidence level. [The SCP was initially set up to test sorbent tubes for sampling accuracy, and since breakthrough was tested separately, sampling non-constant concentrations was not deemed necessary. See BARTLEY *et al.* (1987) for further discussion of this issue.] The bias would, of course, be more acceptable in the sampling of other vapours more tightly bound to the activated charcoal.

Liquid sorbent

The experiments using GMD liquid sorbent samplers (Fig. 3) were somewhat similar to the above experiment with activated charcoal, except that water was used as the sorbent. To cover a range of phenomena, acetone (with a high vapour pressure over water solutions) and methanol (relatively low vapour pressure) were selected as analytes. Note that the acetone–water system was intentionally selected to obtain an analyte loss effect (i.e. because acetone has a relatively high vapour pressure above aqueous solution, another sorbent with a higher affinity for acetone would normally be chosen for use in a practical sampling application).

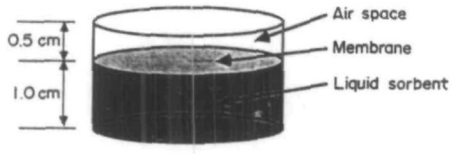

FIG. 3. Schematic of GMD liquid-sorbent sampler.

The first experiment entailed a direct measurement of acetone loss. Ten samplers were initially filled with an aqueous solution of 100 ppm acetone. This large initial concentration was selected for analytical accuracy and in light of the fact that a linear sampler [Equation (1)] is subject to identical rates and biases at lower concentrations. The samplers then were placed in acetone-free air circulating at 100 cfm. Samplers were capped and removed at 30, 60, 120 and 240 min following spiking. Residual acetone concentrations in the badges were then measured by gas chromatography.

The data from this experiment and the (residual) errors between the model of Equation (4) and the data are shown in Fig. 4. The initial concentration C_0, the coefficient of diffusion D' for acetone in water, and a combination of Henry's law constant H and the front membrane permeability were allowed to vary until a best fit was obtained. The best value for the diffusion coefficient D' was

$$D' = (1.5 \pm 0.3) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1},$$

which may be compared with a published (KAMEI *et al.*, 1970) value of $(1.4 \pm 0.3) \times 10^{-5}$ cm^2 s^{-1}.

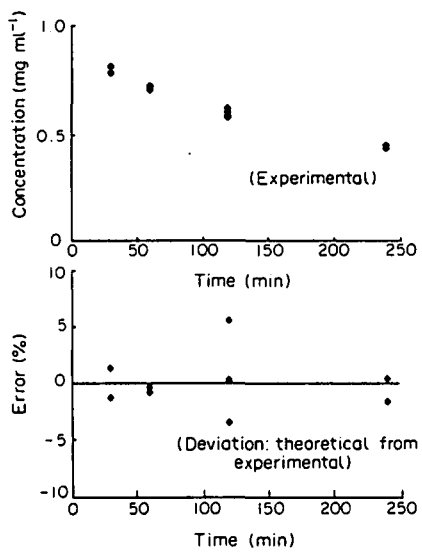

FIG. 4. Loss of acetone from several samplers with identical initial concentrations. (Data scatter is partially due to inter-sampler variation in diffusion length between sorbent and external air.) Goodness of fit of theoretical model to the experimental data is also shown.

The parameters determined by the above data were then used to predict the results of a separate experiment very similar to the activated charcoal experiment described earlier. Six samplers were exposed to 200 ppm acetone in air for 1 h and then removed from the exposure chamber. Two samplers were closed immediately, two after 1 h in acetone-free air, and two after 3.5 h.

The results are shown in Fig. 5 together with predictions from the theoretical model given in Equation (4). Agreement between theory and experiment indicates that the tenets of the theory are basically correct. Note the two-fold range in the measured

values of the collected mass, even though the true time-weighted average is constant. This bias in sampling time-dependent concentrations is therefore even larger than in the activated charcoal experiment and does not meet the NIOSH Standards Completion Programme standards.

A separate experiment on GMD sampler loss of methanol was also conducted. As the Henry's law constant for methanol is an order of magnitude higher than that of acetone, diffusion within the liquid has more time to keep the liquid sufficiently mixed so as to maintain a homogeneous methanol concentration. (The methanol and acetone diffusion rates are roughly equal.) In this case, analyte is lost simply exponentially in time as in Equation (11).

Figure 6 gives data from the corresponding experiment. Six samplers were filled with an aqueous methanol solution at an initial concentration of 0.94 mg ml^{-1}. Following exposure to clean air, two of the samplers were closed at 120 min, two at 240 min and two at 360 min and the remaining methanol concentrations measured. The theoretical curve was calculated from Equation (11), using a sampling (in this case, loss) rate $[DA/L] = 50$ ml min^{-1}, as suggested in the GMD instruction manual. The data indicate that the exponential model is adequate for describing this sampling system.

RECOMMENDATIONS

The above experiments using two types of passive samplers employing thick sorbents indicate the possibility of a sampling bias specific to diffusive gas or vapour samplers. Namely, if the analyte is weakly bound to the sorbent, material can be lost to the atmosphere. Although a significant thickness of the sorbent introduces a degree of mathematical complexity, the basic problem in analysing time-varying concentrations remains.

To help safeguard against such problems, a general screening performance test can be applied to identify samplers with overly variable sampling rates. The philosophy behind such a test is to challenge prospective samplers to the extreme concentration time-dependencies expected in a workplace environment. In short, if concentrations in a specific workplace can be approximated by superimposing pulses of given duration Δt, then the extreme time-dependencies correspond to single Δt-pulses at the beginning or end of the sampling period. A possible performance test of this type has been

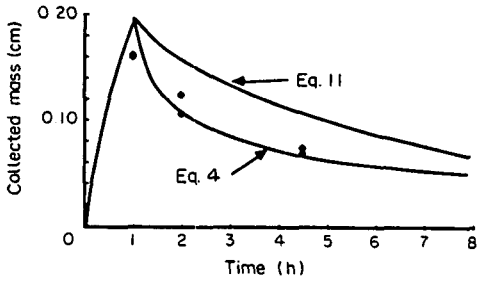

FIG. 5. Measured acetone mass (divided by $[HA \times$ peak concentration$]$) collected in unstirred sampler exposed to a 1 h acetone pulse followed by acetone-free laboratory air. Theoretical prediction (solid curve) according to Equation (4) is based on a best fit to the data of Fig. 4. Note the inadequacy of the exponential loss model of Equation (11) (also shown) with analyte weakly bound to sorbent (as acetone is to water).

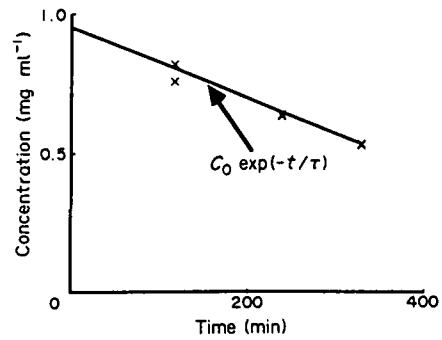

FIG. 6. Loss of methanol from six samplers (overlapping points at 240 and 360 min) with identical initial concentrations. Note the close fit of the exponential decay model.

suggested recently (BARTLEY *et al.*, 1987). Such a test is, of course, more demanding than tests (EINFELD, 1983) employing pulse trains, which accomplish little more than do constant-concentration tests and do not really challenge a sampler's utility in sampling non-constant concentrations.

We believe that the diffusive monitor has many advantages over pump-based samplers. Worker acceptance, maintenance simplicity and the absence of sampling errors due to pump variations are very attractive features of this sampling system. In focusing on potential problems specific to this type of sampler, we hope to point out situations in which the use of such monitors may be inappropriate so that informed decisions can be made about their general application to industrial hygiene sampling.

REFERENCES

ABRAMOWITZ, M. and STEGUN, I. A. (1964) *Handbook of Mathematical Functions*. Dover Publications, New York.

BARTLEY, D. L. (1983) Passive monitoring of fluctuating concentrations using weak sorbents. *Am ind. Hyg. Ass. J.* **44**, 879–885.

BARTLEY, D. L. (1986) Diffusive samplers using longitudinal sorbent strips. *Am. ind. Hyg. Ass. J.* **47**, 571–577

BARTLEY, D. L., DEYE, G. J. and WOEBKENBERG, M. L. (1987) Diffusive monitor test: performance under transient conditions. *Appl. ind. Hyg.* **2**, 119–122.

BARTLEY, D. L., DOEMENY, L. J. and TAYLOR, D. G. (1983) Diffusive monitoring of fluctuating concentrations. *Am. ind. Hyg. Ass. J.* **44**, 241–247.

BERTONI, G., PERRINO, C., FRATARCANGELI, R. and LIBERTI, A. (1985) Critical parameters for the adsorption of gaseous pollutants on passive samplers made of low specific area adsorbents. *Anal. Lett.* **18**, 429–438.

BROWN, R. H., CHARLTON, J. and SAUNDERS, K. J. (1981) The development of an improved diffusive sampler. *Am. ind. Hyg. Ass. J.* **42**, 865–869.

COUTANT, R. W., LEWIS, R. G. and MULIK, J. (1985) Passive sampling devices with reversible adsorption. *Anal. Chem.* **57**, 219–223.

COX, P. C. and BROWN, R. H. (1984) A personal sampling method for the determination of nitrous oxide exposure. *Am. ind. Hyg. Ass. J.* **45**, 345–350.

CRANK, J. (1975) *The Mathematics of Diffusion*. Clarendon Press, Oxford.

EINFELD, W. (1983) Diffusional sampler performance under transient exposure conditions. *Am. ind. Hyg. Ass. J.* **44**, 29–35.

FEIGLEY, C. E. and CHASTAIN, J. B. (1982) An experimental comparison of three diffusion samplers exposed to concentration profiles of organic vapors. *Am. ind. Hyg. Ass. J.* **43**, 227–234.

GONZALEZ, L. A. and SEFTON, M. V. (1983) Stain length passive dosimeter for monitoring of carbon monoxide. *Am. ind. Hyg. Ass. J.* **44**, 514–520.

GREGORY, E. D. and ELIA, V. J. (1983) Sample retentivity properties of passive organic vapor samplers and charcoal tubes under various conditions of sample loading, relative humidity, zero exposure level periods and a competitive solvent. *Am. ind. Hyg. Ass. J.* **44**, 88–96.

GUNDERSON, E. C. and ANDERSON, C. C. (1980) *Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances*. DHHS (NIOSH), Publication No. 80–133. Cincinnati, Ohio, U.S.A.

HEARL, F. J. and MANNING, M. P. (1980) Transient response of diffusion dosimeters. *Am. ind. Hyg. Ass. J.* **41**, 778–783.

HINE, J. and MOOKERJEE, P. K. (1975) The intrinsic hydrophilic character of organic compounds. Correlations in terms of structural contributions. *J. Org. Chem.* **40**, 292–297.

KAMEI, YOSHINOBU, OISHI and YASUICHI (1970) Self-diffusion coefficient of water and acetone in the water-acetone system. *Nippon Kagaku Zasshi* **91**, 403–404.

POSNER, J. C. (1981) Letter to the Editor. *Am. ind. Hyg. Ass. J.* **42A**, 28–30.

POSNER, J. C. and MOORE, G. (1985) A thermodynamic treatment of passive monitors. *Am. ind. Hyg. Ass. J.* **46**, 277–285.

SOMMERFELD, A. (1964) *Partial Differential Equations in Physics*. Academic Press, London.

UNDERHILL, D. W. (1983) Unbiased passive sampling. *Am. ind. Hyg. Ass. J.* **44**, 237–239.

APPENDIX

MATHEMATICAL CONSIDERATIONS

Terminology

A	cross-sectional area (cm^2) of sampler
β	frequency (s^{-1}) defined by D'/l^2
$C(z, t)$	concentration (g cm^{-3}) at distance $-z$ from sorbent at time t
$C_{ext}(t)$	external analyte concentration (g cm^{-3}) in atmosphere at time t
d	sorbent thickness (cm)
D	diffusion constant (cm^2 s^{-1}) in air
D'	diffusion constant (cm^2 s^{-1}) within sorbent
$G(z, t)$	Green's function for analyte concentration within sampler
$g(t)$	sampler response function
H	Henry's law constant (unitless)
L	length (cm) of air space between atmosphere and sorbent
l	length (cm) defined as LHD'/D
$m(t)$	analyte mass (g) within sampler at time t
ρ	analyte concentration (g cm^{-3}) in sorbent
t	time (s)
t_s	sampling period (s)
τ	loss time (s) from well-mixed sampler ($= VH/[DA/L]$)
τ_{trans}	time (s) required for transients to disappear within sorbent
z	distance (cm) along sampler
V	sorbent volume (cm^3)

General case

Let z denote distance along the tube, $z = d$ denoting the closed end (or, in the case of the ORSA 5, the midpoint) of the tube, $z = 0$ representing the other end of the sorbent column, and $z = -L$ referring to the open end of the tube exposed to the external concentration C_{ext}. Then assuming rapid decay of transients in the air space or front membrane, the concentration at $z \leq 0$ is simply linear in z. Therefore, the slope $\partial C/\partial z$ of the concentration is given by

$$\partial C/\partial z = (C(0) - C_{ext})/L \qquad -L \leq z \leq 0. \tag{A1}$$

The density of analyte ρ within the sorbent at the sorbent end ($z = 0$) is assumed to be proportional to the local concentration C in the air space:

$$\rho = HC, \tag{A2}$$

where H is the Henry's law constant. Furthermore, diffusion of analyte within the sorbent is characterized by (an often extremely small) diffusion constant D' via:

$$\partial \rho/\partial t = D' \partial^2 \rho/\partial z^2. \tag{A3}$$

Mixed boundary conditions on ρ at $z = 0$ therefore are obtained from Equations (A1)–(A3) as:

$$\rho - l \partial \rho/\partial z|_{z=0} = HC_{ext}, \tag{A4}$$

where the length l is defined as

$$l = LHD'/D. \tag{A5}$$

At the closed end of the sampler ($z=d$) the mass flux is zero:

$$\partial\rho/\partial z|_{z=d}=0. \tag{A6}$$

Equations (A3)–(A6) together with the initial conditions [e.g. $\rho(z)=0$ for all z at $t=0$] completely determine $\rho(z, t)$ in terms of the external concentration $C_{ext}(t)$. Using methods described in the literature (SOMMERFELD, 1964; CRANK, 1975), $\rho(z, t)$ may be expressed in terms of a Green's function G in the form

$$\rho(z,t)=(HD'/l)\int_0^t dt' G(z, 0; t-t')C_{ext}(t'). \tag{A7}$$

The mass $m(t_s)$ sampled prior to time t_s is related to the density $\rho(z,t_s)$ by

$$m(t_s)=A\int_0^\infty dz\rho(z, t_s), \tag{A8}$$

which may be expressed in terms of a response function g as in Equations (2) and (3) of the text.

Infinite sorbent

If the sorbent is long, i.e. if $d=\infty$, then the Green's function $G(z, z'; t)$ for use in Equation (A7) is given (SOMMERFELD, 1964) by

$$(4\pi D't)^{1/2}G(z, z'; t)=\exp[-(z-z')^2/(4D't)]+\exp[-(z+z')^2/(4D't)]$$
$$-2l^{-1}\exp(z'/l)\int_{-\infty}^{-z'} d\zeta\ \exp[-(z-\zeta)^2/(4D't)]\exp[\zeta/l]. \tag{A9}$$

Using Equation (A9) and carrying out one of the integrations of Equation (A8) results in the sampler response function given in Equation (4).