Passive Monitoring of Fluctuating Concentrations Using Weak Sorbents

DAVID L. BARTLEY

Passive Monitoring of Fluctuating Concentrations Using Weak Sorbents

DAVID L. BARTLEY, Ph.D.

National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226

Diffusive monitoring of fluctuating concentrations is analyzed for the situation in which the concentrations of each component of a mixture to be sampled do not necessarily remain close to zero at the sorbent surfaces. Considering first samplers with a single sorbent surface, an estimate of time weighted averages (TWA) of the concentration in terms of measured mass is given which is unbiased in the limit of small concentrations. Bounds on the fluctuation-related error in this estimate are derived which may be calculated from the collected masses of any given sample. The error limits relate to both linear as well as leading non-linear regions of the empirical sorbent isotherm. The error limits imply potentially excessive error in the estimation of concentrations over averaging times as long as 8 hours. Reduction of this error and detection of breakthrough through the use of multiple sorbent surfaces is discussed.

Introduction

Passive samplers have found increasing use in the past few years in the monitoring of hazardous substances. Nevertheless, several questions as to sampler reliability remain, and the aim of the present paper is to address one of these potential problem areas. Rather than using a pump, passive devices rely on diffusion to provide a flux of material into the sampler. Because diffusion is generally a slow process, the question arises as to the accuracy of using passive samplers in the estimation of time weighted averages (TWA) of concentrations which may be changing in time. This includes situations where both worker and source are mobile.

Research on this problem is reported[1,2] where the concentration of the contaminant near the sorbent surface is zero. This is the case with samplers, such as the Palmes tube[3-4], which employ a chemisorbent with low activation energy. The relaxation time t_r required for the disappearance of spatial inhomogeneities in the concentration gradient is given[1-2] by

$$t_r = L^2/(\pi^2 D) , \qquad (1)$$

where L is the sampler length and D is the analyte diffusion constant. For example, for sampling NO_2 with a Palmes tube, L = 7.0 cm and D = 0.15 cm^2/sec; therefore, Equation 1 implies that t_r = 33 sec. The significance of the smallness of t_r is that for most fluctuating concentrations to be found in the workplace, the Palmes tube gives accurate estimates of the time weighted average of the concentration in sampling over entire 8-hour work periods. On the other hand, excessive errors in exposure estimates can be expected in *short* time Palmes tube sampling of some realistic time-dependent concentrations, such as in the measurement of substances with short term exposure limits (STEL). For such situations, a second sorbent surface can be used[2] to eliminate error due to concentration variations.

In the present paper, samplers are considered with such small values of L that approach to spatially constant concentration gradients can be considered to occur instantane-ously, even in STEL sampling. As a concrete model of such a sampler, the Du Pont Pro-Tek G-BB sampler[5], which consists of two activated carbon sheets of width 0.058 cm separated (center to center) by L_1 = 0.401 cm and from the atmosphere by L_2 = 0.373 cm will be used throughout this paper. See Figure 1 for a stylized version of this sampler. Equation 1 implies that the relaxation time t_r is about two orders of magnitude shorter for such a sampler than the Palmes tube. Therefore, even within STEL sampling, the approximation of homogeneous concentration gradients is valid.

Unfortunately, this does not imply that there are no fluctuation-associated errors in sampling with this type of monitor. This is because the analyte-carbon bonds are not strong enough[6] to maintain zero concentration near the sorbent surfaces. The sampling rate, therefore, depends on the amount of material already adsorbed. This is further
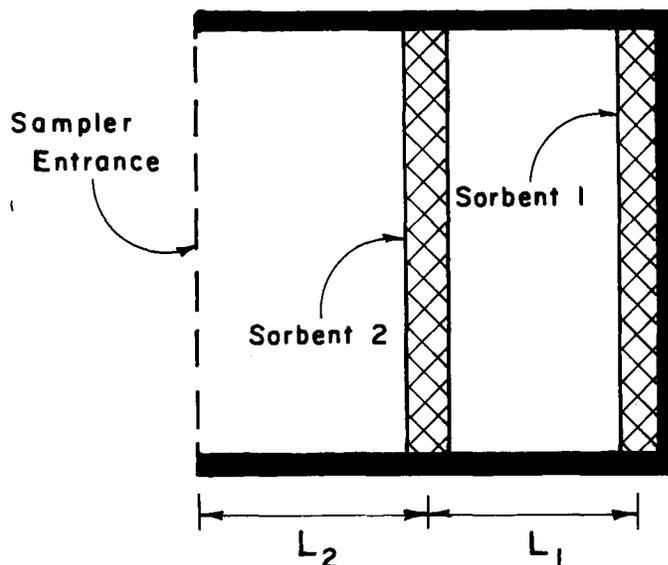

Figure 1 — Two stage diffusive sampler. Note order of dimen-sion numbering.
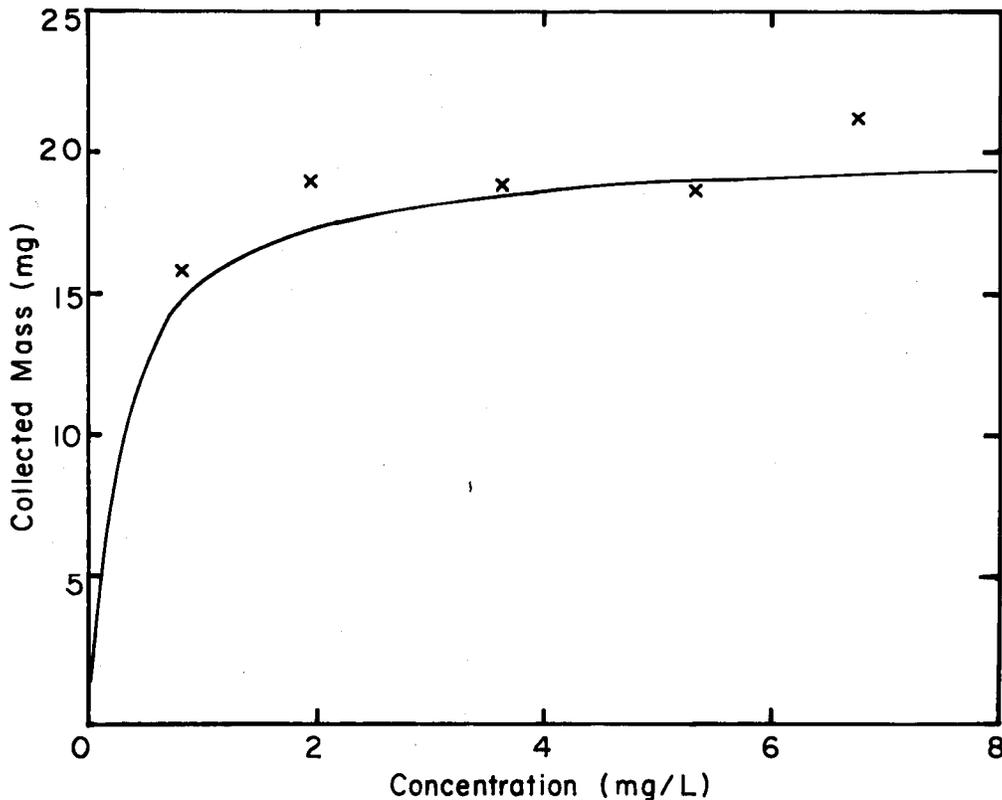
Figure 2 — Experimental[8] adsorption isotherm for methyl chloroform on 300 mg Du Pont Pro-Tek activated carbon at 298°K, 760 mm Hg and 70% relative humidity. Solid line indicates empirical Langmuir isotherm.

complicated because the relation between the concentration at the adsorbent and mass adsorbed may be strongly non-linear. See, for example, Figure 2, which represents this relation as measured[8] for methyl chloroform at 298° K and 70% relative humidity on the Pro-Tek sorbent sheet mentioned above. These data may be represented by an expression in the form given by Langmuir[7],

$$C_j = a^{-1}m_j/(1 - m_j/m_{sat}) , \qquad (2)$$

where m_j and C_j are the adsorbed mass and concentration at the j-th sheet, and Henry's law constant a = 66.6 L and the saturation mass m_{sat} = 20 mg are chosen to make rough fit to the data[8]. (Note that Equation 2 is an empirical model for application over a limited range of masses and does not preclude singular behavior for concentrations very close to zero.)

The present work indicates potential problems with single stage weak sorbent samplers. However, it is shown that the design and control of samplers for adequate TWA concentration estimation is feasible through the use of *multiple* sorbent stages, initially proposed[5] as a means of extending sampling time and also for the detection of breakthrough.The present paper places breakthrough detection on a quantitative footing. Namely, it is shown for arbitrary fluctuation that bounds on the accuracy of the TWA concentration estimate may be calculated given measured adsorbed masses from each stage of an appropriately characterized sampler. This result is found to hold for the sampling of mixtures as well as single analytes. Furthermore, aside from extending

sampling time and breakthrough detection, the extra degree of freedom afforded by the backup surface measurement is found to be useable in minimizing errors specifically related to non-constancy of the concentration.

Single-stage Sampler

Prior to describing the use of multiple surfaces, details are presented for samplers in which only a single adsorbent surface is used. This discussion is interesting in its own right as there exist many such samplers in use at the present time. Furthermore, the results are directly applicable to analysis of multi-stage samplers in which the concentration may be low at one of the stages. At such a surface only effects on sampler performance associated with the linear and leading non-linear parts of the adsorption isotherm (Equation 2) require accounting.

Analysis of the single-stage sampler may be summarized as follows. Neglecting non-linear effects, sampler calibration is derived to provide TWA concentration estimates which are unbiased. Limits on the error in the estimate are then derived for an arbitrary fluctuation. Finally, leading non-linear shifts of the error limits are calculated. Mathematical details not needed for following the main arguments are provided in the *appendix*.

Mass Accumulation Rate

The expression for the rate dm_1/dt of mass accumulation per unit time at the adsorbent surface is very simple within the assumption (unlike the situation investigated in References 1-2) that the sampling length L_1 is small enough that the

concentration varies nearly linearly from point to point within the sampler. In this case the sampling rate is given by

$$dm_1/dt = (AD/L_1)(C_2 - C_1) , \tag{3}$$

where A is the cross-sectional area of the sampler, and $C_2 = C(t)$ the concentration of the analyte in the atmosphere at time t. Note that the assumption has been tacitly made that the sorbent may be approximated as a surface at some point within the sampler. Equation 3 may be expressed entirely in terms of the accumulated mass m_1 by using Equation 2:

$$t_1 dm_1/dt + m_1/(1 - m_1/m_{sat}) = aC(t) , \tag{4}$$

where the relaxation time t_1 for approach to equilibrium with a vanishingly small concentration C(t) is defined as

$$t_1 = aL_1/(AD) . \tag{5}$$

Because Equation 4 is non-linear, closed form solutions are available only for special cases of the function C(t). For example, if the concentration C is a constant, Equation 4 can be integrated and the resultant transcendental equation solved for $m_1(t)$ by iteration using a programmable calculator. The results of such a calculation may be seen in Figure 3 for a single stage Du Pont Pro-Tek device used in sampling 400 ppm methyl chloroform (the concentration and analyte common to References 5 and 7). A value of AD = 0.171 cm⁴/sec, obtained as described below from the data of Reference 5, was used for this calculation. The sampler surfaces approach equilibrium with the external atmosphere over the course of a day of sampling. Therefore, significant errors in concentration estimates might be expected in the sampling of concentrations fluctuating about the above value. For comparison Figure 2 also shows the mass which would be

accumulated were the amount of activated carbon doubled and the sampling length held constant at L_1 = 0.373 cm.

Calibration Theory

If the accumulated mass m_1 is sufficiently smaller than m_{sat} that the linearized version of Equation 4 is valid, then useful general solutions may be found. The linear part of Equation 4 is obtained simply by approximating the denominator $(1 - m_1/m_{sat})$ by 1:

$$t_1 dm_1/dt + m_1 = aC(t) . \tag{6}$$

The general solution of this equation may be expressed in the form,

$$m_1(t) = \int_0^t dt' g(t,t')C(t') , \tag{7}$$

where the response function g(t,t') is given by

$$g(t,t') = (a/t_1)\exp[-(t - t')/t_1] . \tag{8}$$

The question now arises as to how to best use the value of the mass $m_1(t_s)$ accumulated during the sampling period t_s to estimate the TWA $\bar{C}$,

$$\bar{C} = (1/t_s)\int_0^{t_s} dt' C(t') . \tag{9}$$

In other words, how is the sampler to be calibrated? The straightforward answer is to calibrate with a constant concentration over t_s. As described in detail in Reference 2, the advantage of this calibration scheme is that in sampling a concentration which varies randomly in time over sampling periods of fixed duration t_s, $(\bar{C})_{est}$ is distributed randomly about the true average concentration $\bar{C}$, depending on the choice of sampling period start time, rather than about some
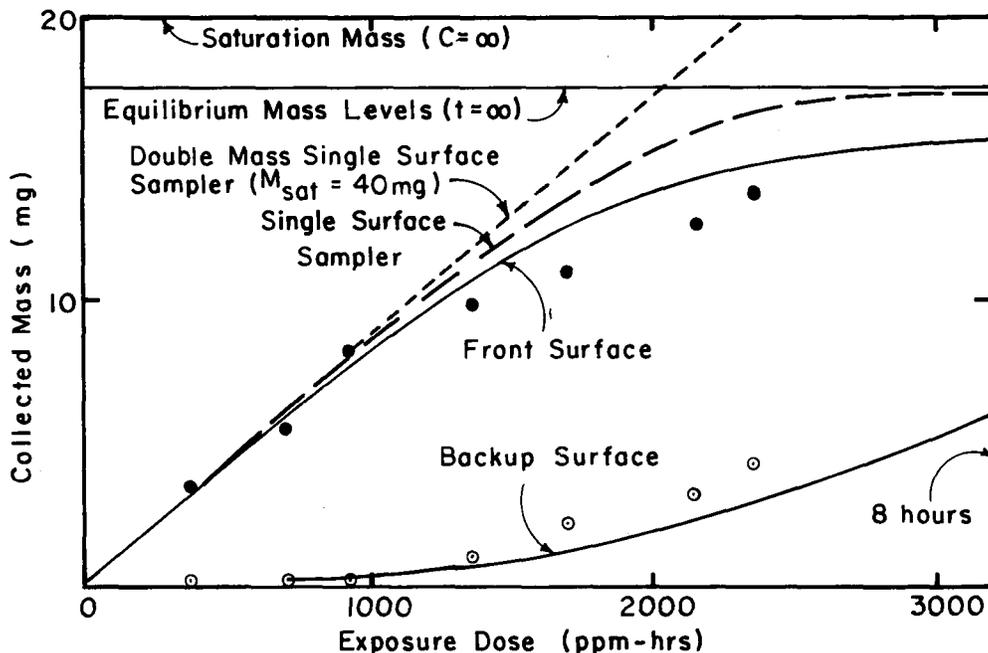

Figure 3 — Mass collected during several types of sampling: 400 ppm methyl chloroform on Pro-Tek activated carbon. Solid curves representing double surface sampler may be compared with data[5] obtained at 298°K, 760 mm Hg and 80% humidity.

other biased value. (For example, since the constant calibration concentration may be represented as a set of pulses uniformly distributed over the sampling period, the average of sampling single pulses located at random within the sampling period will equal the true time average of the pulse.) Therefore, the estimate $(\overline{C})_{est}$ which is unbiased is given by

$$(\overline{C})_{est} = k\, m_1(t_s) \ , \tag{10}$$

where the calibration constant k is obtained by integration of Equation 7 at constant C:

$$k^{-1} = \int_0^{t_s} dt' g(t_s, t') \tag{11}$$

$$= a[1 - \exp(-t_s/t_1)] \ . \tag{12}$$

Error Bounds Within Linear Approximation
Limits can now be calculated for the relative error Δ_1 between $(\overline{C})_{est}$ and $\overline{C}$ defined as

$$\Delta_1 = [(\overline{C})_{est} - \overline{C}]/\overline{C} \ . \tag{13}$$

Unlike the case treated in Reference 2, both upper and lower limits on Δ_1 are finite. As shown in the *appendix,* Δ_1 is confined to:

$$[1 + t_s/t_1 - \exp(+t_s/t_1)]/[\exp(+t_s/t_1) - 1]$$
$$\leq \Delta_1 \leq \tag{14}$$
$$[1 - t_s/t_1 - \exp(-t_s/t_1)]/[\exp(-t_s/t_1) - 1] \ .$$

If adsorption at the activated carbon is strong enough that t_s/t_1 is much smaller than unity, then Equation 14 may be approximated by the extremely simple expression,

$$|\Delta_1| \leq t_s/(2t_1) \ . \tag{14'}$$

For example, $t_s = 28\ 800$ sec corresponds to an 8 hour sampling period, and for methyl chloroform ($L_1 = 0.373$ cm), $t_1 = 145\ 000$ sec; therefore, $t_s/t_1 = 0.20$.

Error Limits Associated with Non-linearities
Equation 14 gives estimates of the error, accounting only for linear effects. In order to calculate the consequence of non-linearities, Equation 4 may be expanded to order $(m_1/m_{sat})^2$:

$$t_1 dm_1/dt + m_1 = aC(t) - (m_1)^2/m_{sat} \ . \tag{15}$$

The non-linearity effected shift from the solution $m_1(t)$ of the linearized equation can be estimated by iteration, substituting into the quadratic term on the right side of Equation 15 and using Equation 7. Calculation along these lines leads to limits on the non-linear contribution Δ_1' to the error. As shown in the *appendix* Δ_1' is confined to

$$-(m_1(t_s)/m_{sat})[\exp(t_s/t_1) - 1] \leq \Delta_1' \leq 0 \ . \tag{16}$$

For t_s much less than t_1, Taylor's series expansion simplifies Equation 16 to

$$-[t_s m_1(t_s)]/[t_1 m_{sat}] \leq \Delta_1' \leq 0 \ . \tag{16'}$$

Equality in the error limits of Equations 14 and 16 is attained when the concentration is non-zero only near the start or finish of sampling.

Example Calculation
Monitoring methyl chloroform using a single Du Pont Pro-Tek sorbent sheet provides a simple example of the use of these limits. With the same parameters as above in sampling for $t_s = 28\ 800$ sec (8 hours), combination of Equations 14 and 16 implies that the error ranges between -30.0% and $+10.0\%$. (Hypothetically) doubling the adsorbent improves matters only slightly: the error is calculated to lie between -18.0% and $+5.0\%$. The sampler seems yet unacceptable, unlike the device proposed in the following section. It must be remarked that because of the uncertainties in the adsorption isotherm at small concentrations (see Figure 2) the specific numbers quoted here are of use mainly in providing an example of the application of the above equations.

Multi-stage Sampler
Error Bounds
At this point it is possible to present a simple analysis of a sampler comprised of a series of adsorbent surfaces. Results are given only for a sampler with two surfaces. However, generalization to n surfaces, which may be useful for analytes only very weakly bound to the sorbent, is straightforward. Suppose the first surface (the "backup surface") is separated from the second by L_1, and the second from the atmosphere by L_2 (Figure 1). Then in addition to Equation 3, there is an equation describing transfer of material from the atmosphere to the second surface and subsequently to the first surface:

$$dm_2/dt = (AD)[(C_3 - C_2)/L_2 - (C_2 - C_1)/L_1] \ , \tag{17}$$

where now $C_3 = C(t)$, the external concentration. The quantity C_1 may be eliminated by adding Equations 3 and 17 with the result:

$$C(t) = C_2 + (L_2/(AD))[dm_1/dt + dm_2/dt] \ . \tag{18}$$

Computing the TWA of $C(t)$ using Equation 18 gives

$$(\overline{C})_{est} = (\overline{C}_2)_{est} + (L_2/(ADt_s))[m_1(t_s) + m_2(t_s)] \ . \tag{19}$$

The only quantity requiring estimation from measured masses on the right side of Equation 19 is $\overline{C}_2$. But estimation of $\overline{C}_2$ is precisely the topic covered in the previous section. Therefore, $(\overline{C}_2)_{est}$ is given by Equation 10 in terms of $m_1(t_s)$, and the linear and non-linear limits on its accuracy may be calculated using Equations 14 and 16 by

$$\Delta = \Delta_1(\overline{C}_2/\overline{C}) \tag{20}$$

$$\Delta' = \Delta_1'(\overline{C}_2/\overline{C}) \ . \tag{21}$$

Note that both factors in Equations 20 and 21 can be small, resulting in further constraint on the overall error. Interestingly, the sampler is easily analyzed, even in cases where the front surface is operating deeply in the non-linear regime. The concentration need be small only at the backup surface for a reasonable analysis of overall accuracy.

For comparison of the single and double sorbent samplers, computations were carried out using methyl chloroform as analyte. By trapezoidal integration, Equations 2, 3 and 17

882

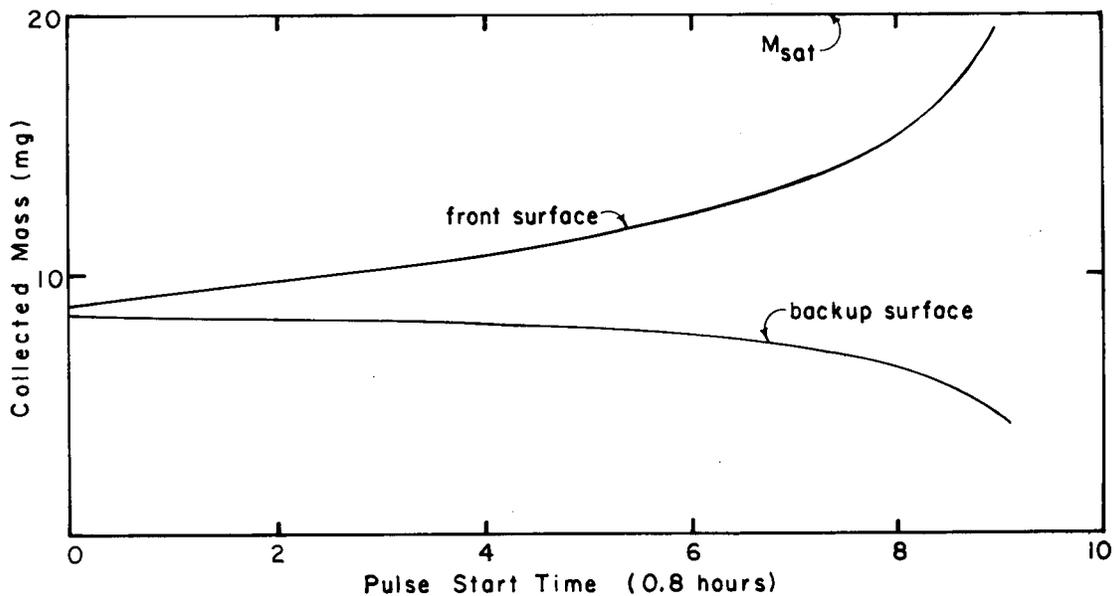*Am. Ind. Hyg. Assoc. J (44)*   December, 1983

Figure 4 — Calculated masses collected by double surface monitor in sampling 0.8 hour pulses of 4000 ppm methyl chloroform in terms of pulse start time.

were solved ($L_1 = 0.401$ cm and $L_2 = 0.373$ cm) at a constant concentration equal to 400 ppm. The calculated values of mass collected at each surface in terms of exposure dose (ppm-hours) are shown in Figure 3. The theoretical curves follow the data of Reference 5 in spite of the large uncertainties in the adsorption isotherm data[8] and the fact that the relative humidity was 10% higher than that of the isotherm experiment. Note that the value of the quantity AD was fixed from the linear portion (low exposure dose) of the data[5].

Example: Sampling a Single Pulse

A more interesting calculation with a time dependent concentration was then carried out. For this purpose, a single square pulse of duration 0.8 hour was used. A magnitude equal to 4000 ppm was selected so as to keep the TWA concentration for 8 hour sampling periods at the same level as in Figure 3. As can be seen in Figure 4, the individual masses collected on the front and back surfaces depend

markedly upon the time (which would generally be unknown in practice) at which the pulse occurs. Nevertheless, the estimated concentration $(\overline{C})_{est}$ given by Equation 19, combining information available in the two measured quantites m_1 and m_2, remains very constant and close to the time weighted average equal to 400 ppm. This may be seen in detail in Figure 5, where the error between estimated and true TWA concentrations is plotted in terms of the pulse start time. Also shown are the upper and lower limits on the error as calculated from the computed values m_1 and m_2 using Equations 20 and 21. The worst-case sample (with pulse at the beginning or end of the sampling period) limits the error between -5.0% and 3.0%, which reflects a marked improvement, through the use of two degrees of freedom, over the single-surface samplers described earlier. Note that the mass collected by the back-up surface can, in some instances, be of the order of that adsorbed at the front surface without invalidating the sample.
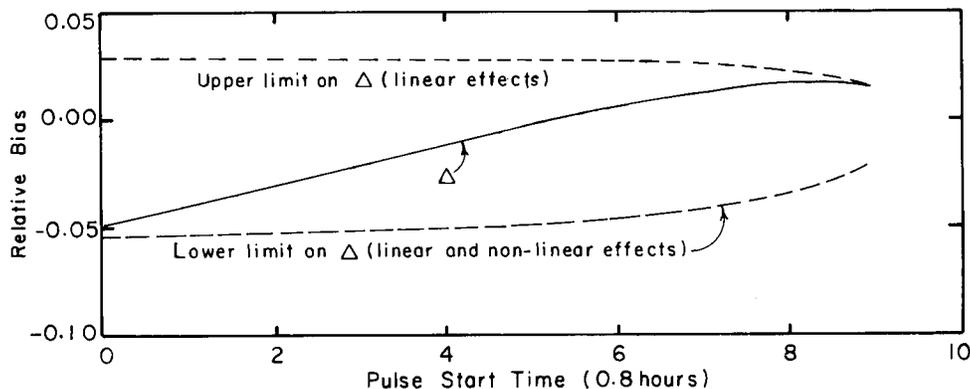

Figure 5 — Relative error Δ in the estimated time weighted averages of concentrations corresponding to the conditions of Figure 4. Dashed curves represent extreme bounds within which the error in the estimate may range, if only the values of the sampled masses are known.

Sampler Characterization

It must be emphasized at this point that during the course of monitor design, the manufacturer would characterize the sampler by direct measurement of sampler response, rather than as in this paper. This is because of uncertainty in the effective sampler dimensions, the diffusion constant and properties of the sorbent. The simplest characterization entails N (≥ 4) determinations of m_1 and m_2 effected by a single concentration pulse of known TWA concentration $\bar{C}$ at time t_p, $p = 1, ..., N$. The pulse must be sufficiently large that the concentration C_1 at the back-up surface is itself pulsed, as in the computer experiment of Figures 4 and 5. Then constants c_1, c_2, c and c' which characterize the sampler would be obtained by using standard statistical techniques to best fit the data by the model:

$$\bar{C} = (\bar{C})_{est} - \bar{C}\Delta_{total}(t_p) , \qquad (22)$$

$$(\bar{C})_{est} = [c_1 m_1 + c_2 m_2]/t_s , \text{ and} \qquad (23)$$

$$\bar{C}\Delta_{total}(t_p) = [cm_1(t_p - t_s/2) - c'm_1^2(t_s - t_p)]/t_s . \qquad (24)$$

(Equation 24 is valid for substances for which $t_s \ll t_1$ as in Equations 14' and 16'.) After such characterization of the sampler, Equation 23 could be used for general concentration estimation with error bounds given by c and c':

$$-cm_1/2 - c'(m_1)^2 \leq \bar{C}\Delta_{total} \leq cm_1/2 . \qquad (25)$$

Multiple Component Sampling

The results presented thus far would find only limited application if generalization to the sampling of a mixture of components were not possible. Fortunately, in the situation that the various components interact only very weakly in the adsorbed state, most of the above formalism carries over directly to mixture sampling. Only a slight change is required in the expression for the non-linear contribution to the error bounds on the concentration estimates. Furthermore, estimation of the error bounds is feasible in practice due to the fact that no further sampler characterization is necessary than as described in the previous section using single analytes.

Generalization to mixture sampling is simple, as Equations 3, 17 and therefore Equation 19 are valid for the concentration of each substance present in the atmosphere. Thus, only the bounds on the estimate $(\bar{C}_{2(i)})_{est}$ in Equation 19 for the i-th component in the mixture are needed in terms of the masses measured on the backup surface. These bounds are slightly different from those calculated above in the section entitled, *"single-stage sampler,"* because competition between components for sites at the backup sorbent renders Equation 2 invalid.

Straightforward statistical mechanical calculation[7], however, gives the generalization of the Langmuir isotherm (Equation 2) for the i-th noninteracting component in the form,

$$C_{1(i)} = (a_{(i)})^{-1} m_{1(i)}/(1 - \nu_1/\nu_{sat}) . \qquad (26)$$

In Equation 26, ν_1 and ν_{sat} are the total and saturated numbers of moles of adsorbed matter at the backup surface.

If ν_1 is sufficiently smaller than ν_{sat}, the right side of Equation 26 may be expanded in the form,

$$C_{1(i)} = (a_{(i)})^{-1} m_{1(i)}(1 + \nu_1/\nu_{sat}) . \qquad (27)$$

In Equation 27 site competition is absent in the linear (first) term and therefore appears only in the non-linear contribution to the error bounds. For estimation of non-linear effects, $m_{1(i)}\nu_1/\nu_{sat}$ in Equation 27 may be expressed in terms of the measured masses $m_{1(j)}$ at the backup surface and their molecular weights $M_{(j)}$:

$$m_{1(i)}\nu_1/\nu_{sat} = m_{1(i)}[\sum_j m_{1(j)}/M_{(j)}]/[m_{sat(i)}/M_{(i)}] \qquad (28)$$

$$= [\sum_j m_{1(i)} m_{1(j)} M_{(i)}/M_{(j)}]/m_{sat(i)} . \qquad (28')$$

Equation 27 implies that the second term of the right side of Equation 15 must be replaced by the expression given by Equation 28' to account for site competition. Derivations following Equation 15 are entirely analogous to those given above for single analyte sampling, however, and therefore generalization of the relevant equations can be carried out easily by inspection.

For example, results for a sampler characterized empirically by constants $c_{1(i)}$, $c_{2(i)}$, $c_{(i)}$ and $c'_{(i)}$ (four constants for each component) are as follows. Equations 22-24 hold, as is, for each component of the mixture. Equation 25 for the bounds on the error $\Delta_{total(i)}$ in the concentration estimate of the i-th component becomes:

$$-c_{(i)} m_{1(i)}/2 - c'_{(i)}[\sum_j m_{1(i)} m_{1(j)} M_{(i)}/M_{(j)}]$$
$$\leq \bar{C}\Delta_{total(i)} \leq \qquad (29)$$
$$c_{(i)} m_{1(i)}/2 .$$

Equation 29 shows that error bounds may be very easily calculated, even for sampling a mixture of substances. The only requirement is suitable sampler characterization by prior experiment with pure analytes. Were it not for this simplification, error estimation would quickly become entirely impractical as the number of substances increases beyond unity.

Conclusions

The ideas considered above indicate potential problems in the diffusive sampling of time-dependent concentrations using surfaces comprised of an imperfect-sink sorbent (such as activated carbon in sampling methyl chloroform). Unless it is known that the concentrations of vapors to be monitored remain sufficiently constant in time, then excessive errors in TWA concentration estimates (averaged, for example, over 8 hours) are possible. For example, in the extreme case in which the concentration rises and falls in the form of a single pulse, the adsorbed mass can be much larger if the pulse arrives near the end of the sampling period than if at the beginning. Following the pulse, the (weak) sorbent supports a small but finite concentration, which drives mass diffusively out of the sampler towards zero ambient concentration. Therefore, although the TWA concentration is *fixed,* a considerable variety of net sampled masses is possible, depending on the time of the pulse occurrence, since the

mass loss depends on the time remaining in the sampling period after the pulse. This effect is exacerbated if the TWA concentration is large, *i.e.*, if the sampler is operated near breakthrough.

A major result of this paper is evidence that this error in TWA concentration estimates may be significantly reduced through the use of several sorbent surfaces in tandem. In this case a pulsed concentration can again leave a variety of sampled masses on the front and back-up surfaces depending on timing. A pulse which occurs near the beginning of sampling can, in some cases, result in roughly equal masses adsorbed at the two surfaces. On the other hand, a pulse near the end of the sampling period may leave the back-up surface nearly untouched. Knowledge of the relative masses on the front and back-up surfaces therefore pinpoints the pulse time, and appropriate corrections for losses from the sorbent surfaces can be made. Extension of this idea implies that the fluctuation related error in TWA concentration estimates may be minimized through the use of back-up surfaces, regardless of the time-dependence of the instantaneous concentration.

Furthermore, calculations given in this paper show that the remaining errors are analyzable. A sampler may be characterized to such an extent that extreme values of the errors in the concentration estimate may be judged for any single set of sampled masses, considering all possible concentration fluctuations. Therefore, even if nothing is known about the instantaneous time dependence of the concentration, the values of the measured sampled masses yield bounds on the possible errors present in the TWA estimates.

These results can be used at the sampler design stage to help ensure that the proposed sampler is capable of whatever degree of accuracy is desired. Furthermore, knowledge of worst-case sampling conditions should find application in the development of performance guidelines and, correspondingly, reasonable tests for sampling method validation. More specifically, in analogy to the detection of breakthrough in sorbent tube sampling, the error limits derived above can be used in quantitative decisions as to the validity of individual samples.

Related areas which require further study are as follows. Experimental verification of the calculations presented in this paper must be carried out. Adequacy of using the Langmuir functional form for the empirical adsorption isotherm could thereby be determined. Relatedly, compounds which interact strongly in the adsorbed state must be identified. Furthermore, discovery of a simple dependence of sampler characterization constants on environmental conditions (*i.e.*, temperature and relative humidity) would be most useful. Finally, diffusive samplers which employ a sizeable length of sorbent should be investigated. Such samplers would seem to combine sampling errors of the type considered in the present paper and those of References 1-2 with the further complication of a changing sampling length.

Clearly there exist important unexplored questions regarding diffusive sampling using weak sorbents. Moreover, the present paper shows that some sampling equipment may lead to concentration estimates dominated by large errors. While (sometimes radical) solutions to these sampling problems are yet to be uncovered, a conservative approach in applying new methods is in order.

References

1. **Hearl, F.J. and M.P. Manning:** Transient Response of Diffusion Dosimeters. *Am. Ind. Hyg. Assoc. J. 41*:778-783 (1980).
2. **Bartley, D.L., L.J. Doemeny and D.G. Taylor:** Diffusive Monitoring of Fluctuating Concentrations. *Am. Ind. Hyg. Assoc. J. 44*:241-247 (1983).
3. **Palmes, E.D. and A.F. Gunnison:** Personal Monitoring Device for Gaseous Contaminants. *Am. Ind. Hyg. Assoc. J. 34*:78-81 (1973).
4. **Palmes, E.D., A.F. Gunnison, J. DiMattio and C. Tomczyk:** Personal Sampler for Nitrogen Dioxide. *Am. Ind. Hyg. Assoc. J. 37*:570-577 (1976).
5. **Lautenberger, W.J., E.V. Kring and J.A. Morello:** *A New Passive Organic Vapor Badge with Backup Capability.* ACS Symp. Series No. 149 (1981).
6. **Posner, J.C.:** Letter to the Editor. *Am. Ind. Hyg. Assoc. J. 42*:A-28 (1981).
7. **Reif, F.** *Fundamentals of Statistical and Thermal Physics.* McGraw-Hill Book Company, London (1965).
8. **Gregory, E.D.:** *An Investigation into Factors Affecting the Performance of Passive Samplers and Charcoal Tubes for Some Organic Vapors*, Ph.D. Thesis. University of Cincinnati, Cincinnati, OH (1982).

APPENDIX

Error Limit Calculations

Limits on the linear contribution Δ_1 are derived as follows. Equation 8 implies that over $0 \leq t' \leq t_s$, the response function $g(t_s, t')$ is minimum at $t' = 0$ and maximum at $t' = t_s$. Therefore, the integral of Equation 7 is subject to the limits:

$$g(t_s, 0)\overline{C}t_s \leq m_1(t_s) \leq g(t_s, t_s)\overline{C}t_s . \qquad \text{(a1)}$$

Equation a1 leads directly to the limits on the error due to linear effects as expressed in Equation 14.

Limits on Δ_1' associated with non-linearities are only slightly more complicated. The shift δm_1 from the solution m_1 (Equation 7) effected by the non-linear term of Equation 15 can be calculated by iteration as described above:

$$\delta m_1 = -(am_{sat})^{-1}\int_0^{t_s} dt'g(t_s, t')[m_1(t')]^2 . \qquad \text{(a2)}$$

A limit on $m_1(t')$ can be derived as follows:

$$m_1(t') = \int_0^{t'} dt''g(t', t'')C(t'') \qquad \text{(a3)}$$

$$\leq \int_0^{t_s} dt''g(t', t'')C(t'') \qquad \text{(a4)}$$

$$= m_1(t_s)\exp[-(t' - t_s)/t_1] . \qquad \text{(a5)}$$

This limit implies a corresponding limit on δm_1:

$$\delta m_1 \geq -[m_1(t_s)]^2/[t_1 m_{sat}]\int_0^{t_s} dt'\exp[-(t' - t_s)/t_1] . \qquad \text{(a6)}$$

This expression then leads to Equation 16.