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EFFECTS OF LINEAR FLOW VELOCITY AND RESIDENCE TIME ON THE RETENTION OF NON-POLAR AQUEOUS ORGANIC ANALYTES BY CARTRIDGES OF TENAX-GC

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SUMMARY

Strong evidence has been obtained which indicates that film diffusion controls the retention of non-polar organics of low aqueous solubility by the sorbent Tenax-GC. Model compounds which have been studied in this context include the four U.S. Environmental Protection Agency priority pollutants *o*-dichlorobenzene, 1,2,4-trichlorobenzene, naphthalene, and hexachloro-1,3-butadiene. The data indicate that compounds such as these have large aqueous retention volumes on this sorbent. Once sorbed, little loss occurs for μg/l concentrations and sample volumes of several liters. Equations are developed which predict the percent recovery as a function of cartridge dimensions and sample volume flow rate.

INTRODUCTION

During recent years, there has been occasional interest expressed in the literature concerning the use of Tenax-GC [porous poly(2,6-diphenyl-*p*-phenylene oxide)] as an adsorbent for the sampling of trace aqueous organics. In studies using solvent extraction as the recovery step, Leoni and co-workers[1,2] have found Tenax-GC to be very retentive for low μg/l levels of several polycyclic aromatic hydrocarbons (PAHs), the polychlorinated biphenyls (PCBs), and a number of pesticides including hexachlorobenzene, DDT, γ-BHC, parathion, and methylparathion. Versino *et al.*[3] also studied the efficiency of adsorption onto Tenax-GC, but they utilized thermal desorption to place the analyte compounds on the gas chromatographic (GC) column. They reported recovery efficiencies of 89, 89, and 99% for ≈20 μg/l levels of aniline, *p*-cresol, and benzene, respectively. Pyridine, *n*-undecane, and phenol gave recoveries of 41, 70, and 45%, respectively. Chesler *et al.*[4] have described a Tenax-GC method involving thermal desorption, but no recovery studies were carried out by these workers.

Despite these favorable early results, prior to the recent work of Pankow and co-workers[5,6], there has been very little additional interest in employing Tenax-GC as an adsorbent in aqueous sampling. Using thermal desorption to transfer analytes

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from sample cartridges to both packed and capillary GC columns. these workers have obtained good recoveries for seven U.S. Environmental Protection Agency (EPA) priority pollutants, including hexachloroethane, *p*-dichlorobenzene, hexachloro-1,3-butadiene, 1,2,4-trichlorobenzene, and 2-chloronaphthalene[5,6].

The general lack of interest in aqueous sampling with Tenax-GC is due in large measure to the commonly held belief that its specific surface area of 19–30 m^2/g[7,8] is too low to provide adequate sorption capacity. Many analysts have chosen to use the much higher specific surface area XAD resins (*e.g.*, 290–300 m^2/g for XAD-2[9] and 750 m^2/g for XAD-7[10]). These resins owe their high surface area to their open macroreticular structure. Thus, the fact that Tenax-GC has nevertheless been shown to be very retentive of non-polar aqueous organics indicates that the adsorption interactions can be very strong. When the *adsorption* step is followed by *thermal desorption* (a sequence termed ATD by Pankow and co-workers[5,6]), these adsorption capabilities are linked with Tenax-GC's thermal stability to yield a very convenient and sensitive analytical method. Considering the low specific surface area of Tenax-GC, however, it is particularly important that a good understanding be obtained of how parameters such as bed volume, linear flow-rate, volume flow-rate, bed retention time, and particle mesh size affect the efficiency of the sorption process.

THEORETICAL

The approach which has been taken by Cropper and Kaminsky[11] and others[12] in analyzing the retention of an analyte by a sampling bed involves the measurement of the retention volume, V_R, and the number of theoretical plates, n, possessed by the bed for the analyte and conditions of interest. The shape and position of the breakthrough curve may then be predicted. When n is small, breakthrough may occur very quickly even though V_R is large. Unfortunately, when n is small and V_R large, both of these parameters are difficult to determine based on the shape and position of a chromatographic peak. (However, since the retention time is a simple function of the partition ratio, k, and since k is related to the distribution coefficient K_D, V_R may be measured *indirectly* by measuring K_D).

One possible reason for low n values would be poor mass transport between the mobile and stationary phases. Earlier results obtained in our laboratory with the model compounds *p*-dichlorobenzene, hexachloro-1,3-butadiene, and 2-chloronaphthalene indicate that n is small with beds of Tenax-GC (35–60 mesh) at flow-rates of the order of ≈ 0.2 bed volumes per sec, and that poor mass transport is responsible. When recovery experiments were carried out by injecting a standard into a water stream which then passed through a series of two Tenax-GC sampling cartridges[5], three observations were made: (1) a portion (10–30%) of the analytes immediately broke through the first cartridge: (2) when additional water was passed through that cartridge, no additional material was lost; and (3) the per cent recoveries obtained were roughly independent of the volume flow-rate over the range 0.25–2.0 cm^3/sec (bed volume 4.5 cm^3).

Our interpretation of these results is that the sorption process is film diffusion controlled. To the extent that the capacity of the bed is not exceeded, the occurrence of breakthrough reflects the lack of sufficient time for all of the analyte molecules to reach the surface of a particle before exiting the sample bed. The fact that we observed no losses from sample cartridges once analyte molecules had sorbed on the particles indicates that these compounds possess large V_R values on Tenax-GC. The fact that the per cent recoveries were roughly independent of the volume flow-rate is interpreted to be the result of the compensating effects of retention time in the cartridge and the thickness of the diffusion layer, δ (cm).

Since n will be small for short beds of Tenax-GC, and since large V_R values may be inferred for the above mentioned compounds, the approach of Cropper and Kaminsky for predicting breakthrough characteristics will be difficult to apply. The approach which we will take for such predictions will be to examine the rate at which diffusion may take place through δ. As originally proposed by Nernst[13], the concept of a diffusion film involves a completely stagnant layer adjacent to the surface of interest. In spite of the simplifications involved, this concept allows diffusion phenomena at interfaces to be modelled very accurately[14]. Typical values for δ are usually of the order of 10^{-3}–10^{-2} cm[14]. In studies of the kinetics of ion exchange in beds of spherical resin beads, Glueckauf[15] has determined the empirical relation

$$\delta = 0.0029/v_s \tag{1}$$

where v_s = "superficial" linear velocity, V/A (cm/sec); V = volume flow-rate (cm^3/sec), and A = bed cross sectional area (cm^2). No matter how slow v_s is, δ cannot exceed the dimensions of the pore, and at very low velocities Glueckauf[15] reasons that δ is an *uncertain* fraction of the particle radius, r (cm), *possibly* $0.2r$. He has therefore suggested that δ may possibly be better represented by eqn. 2:

$$\delta = 0.2r/(1 + 70rv_s) \tag{2}$$

If the sorption process onto Tenax-GC particles is controlled by diffusion through δ to the particle surfaces, the per cent adsorption (recovery) can be predicted.

Let dx (cm) be the distance which the fluid moves in the bed in the time element dt (sec). If p is the porosity (dimensionless) of the bed, then the void volume element of fluid in the bed is given by $pA\mathrm{d}x$. By Fick's First Law, the flux F (mass per cm$^2 \cdot$ sec) through δ to the surfaces of the particles which are at a distance x from the head of the column will be given by

$$F(x) = \frac{D}{\delta}\left[c_b(x) - c_s(x)\right] \tag{3}$$

where D, $c_s(x)$, and $c_b(x)$ represent the diffusion coefficient (cm^2/sec) of the analyte, the concentration (mass per cm^3) of the analyte in the liquid at the sorbent surface, and the concentration of the sorbing analyte in the bulk liquid phase, respectively.

Since each particle will be in contact with a number of other particles (twelve contact points in the case of a bed of uniform spheres), Glueckauf[15] recommends that the available per particle surface area participating in diffusion transport in chromatographic beds be taken as $2\pi r^2$ rather than $4\pi r^2$. Let z be the number of particles per cm of the bed [$z = 3(1 - p)A/4\pi r^3$ cm^{-1}]. Let $c_s(x)$ be zero for all x (perfect sink, *i.e.*, high V_R). Further, let us focus on the behavior of the concentration of a slug of analyte which, to a first approximation, is passing through the bed in plug flow with no dispersion. (Given the perfect sink assumption which has already been made, challenging the bed with a constant concentration of analyte is equivalent to a continuous series of slugs in plug flow.)

As the plug moves through the bed, the time rate of change of concentration of the plug in the void volume element $pA\mathrm{d}x$ will be:

$$\frac{\mathrm{d}c_b(x)}{\mathrm{d}t} = \frac{-Dc_b(x)\,2\pi r^2 z\,\mathrm{d}x}{\delta pA\mathrm{d}x} \tag{4}$$

Eqn. 4 may be integrated between the limits $c_b = c_i$ when $t = 0$ and $c_b = c_e$ when $t = \tau$ where c_i is the influent concentration of the analyte in the plug, c_e is the effluent concentration of the analyte in the plug, and τ is the residence time of the plug in the bed ($\tau = pAL/V$). The result is:

$$c_e = c_i\,\mathrm{e}^{-3D(1-p)\tau/2pr\delta} \tag{5}$$

The fractional recovery, R, will be given by $(1 - c_e/c_i)$, or:

$$R = 1 - \mathrm{e}^{-3D(1-p)\tau/2pr\delta} = 1 - \mathrm{e}^{-3D(1-p)AL/2Vr\delta} \tag{6}$$

Eqns. 1 and 6 demonstrate that R can be independent of V when using a bed of fixed dimensions. A large value of V will imply a small δ value, but a short residence time τ as well. Conversely, lower V values increase δ and slow down diffusion, but an increasing residence time τ can compensate and thereby tend to hold R constant.

The recoveries which may be expected with a 7.0 × 0.94 cm I.D. bed packed with monodisperse, spherical, perfect sink particles have been calculated by eqn. 6 for several r values in the 35–60 mesh range. Diffusion coefficients for non-ionic organic compounds of intermediate size are of the order of 8×10^{-6} cm^2/sec[16], and that value has been assumed for D. A value of 0.38 has been taken for p[17]. The three straight lines (A–C) and the three curves (D–F) in Fig. 1 were calculated assuming that δ is given by eqns. 1 and 2, respectively. Lines A–C were terminated at low v_s when eqn. 1 gave a δ value less than $0.2r$.

The experimental values plotted were obtained with Tenax-GC beds of the same dimensions and packed with non-spherical particles in the 35–60 mesh range[5]. Since these R values are close to 1.0, the uncertainty of perhaps ±5% in the data for p-dichlorobenzene and hexachloro-1,3-butadiene makes it difficult to determine whether the functionality of eqn. 1 or that of eqn. 2 is more appropriate in setting δ in these cartridges. However, the data for 2-chloronaphthalene demonstrate a slight dependence on v_s similar to that expected based on eqn. 2. This may be significant since the perfect sink assumption is probably most appropriate for this compound (of the three, it has the greatest GC retention time on Tenax-GC), and subsequent work in our laboratory has indicated that the analytical data were probably most accurate for 2-chloronaphthalene. The early work of Leoni and co-workers[1,2] may also be understood in terms of eqn. 6. Those workers employed 1.5 g of Tenax-GC (60–80 mesh) in a 8 × 1 cm I.D. bed with a volume flow-rate of ≈0.8 cm^3/sec. If D, p, and r

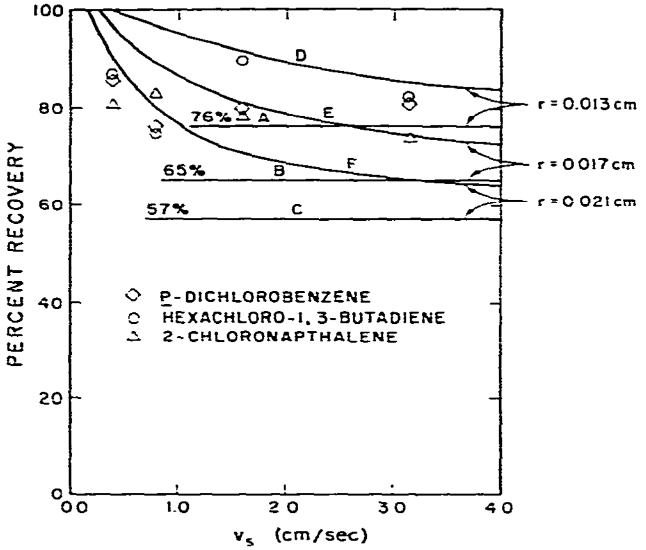

Fig. 1. Per cent recovery as a function of v_s. Experimental data taken from Pankow and Isabelle[5]. Theoretical R values calculated using eqn. 1 (lines A–C) and eqn. 2 (curves D–F). r values of 0.013 and 0.021 cm correspond to 60 and 35 mesh, respectively.

values of 8×10^{-6} cm^2/sec, 0.38, and 0.011 cm are chosen, eqns. 2 and 6 predict an R value of 0.99. This is in good agreement with their reported R values of ≈ 0.95 for a variety of pesticides and PAHs.

In order that the great potential of Tenax-GC as an adsorbent in aqueous sampling may be maximized, a deconvolution of the τ/δ effects is needed. It may be accomplished by examining the recoveries observed with two series of cartridges: in the first, τ is held constant and v_s is varied; in the second, τ is varied and v_s is held constant. This deconvolution will allow sampling cartridge dimensions and sampling flow-rates to be selected so as to provide the maximum recovery with the minimum of analysis time.

EXPERIMENTAL

Cartridge preparation

Glass cartridges with five different I.D.s and bed lengths were prepared (Table I). Cartridge types 1, 2, and 3 provide a series of increasing τ values while maintaining v_s constant, and cartridge types 4, 2, and 5 provide a series with increasing v_s values with τ maintained constant. A 1.5-cm piece of 2.0 mm I.D., 6.4 mm (0.25 in.) O.D. glass tubing was fused to each end of all of the cartridges. Glass wool was placed at the bottom of each cartridge. The cartridges were then packed with resieved Tenax-GC (35–60 mesh) (Alltech, Los Altos, CA, U.S.A.). After passing a 20 cm^3/min flow of N_2 (pre-cleaned with charcoal and molecular sieve 5A (Chemical Research Services, Addison, IL, U.S.A.) for 60 min to remove oxygen, the cartridges were conditioned for 60 min at 280°C. They were then cooled quickly, removed from the N_2 flow, and sealed with 0.25-in. Swagelok (Crawford Fitting, Solon, OH, U.S.A.) end

TABLE I

CARTRIDGE DIMENSIONS

τ values calculated assuming a porosity, p, of 0.38. Volume flow-rate, V, was 0.48 cm^3/sec in every case.

Cartridge type	*I.D. (cm)*	*A (cm^2)*	*L (cm)*	*Bed volume (cm^3)*	*Tenax-GC (g)*	*v_x (cm/sec)*	*τ (sec)*
1	0.69	0.37	3.0	1.1	0.19	1.28	0.88
2	0.69	0.37	6.0	2.2	0.38	1.28	1.74
3	0.69	0.37	10.0	3.7	0.63	1.28	2.93
4	0.94	0.69	3.2	2.2	0.38	0.70	1.74
5	0.55	0.24	9.2	2.2	0.38	2.00	1.74

caps with TFE Teflon® ferrules. Although not employed in this study, the passage of a large number of bed volumes of acetone through the cartridges prior to the thermal conditioning step is very helpful in lower overall blank levels.

Recovery tests, cartridge desiccation, and cartridge desorption

The apparatus used in the recovery tests was composed of a pressurized water reservoir, an injection port, and a glass wool cartridge for good mixing. The Tenax-GC cartridge to be tested was connected with a 0.25 × 0.25 in. Teflon Swagelok union to the glass wool cartridge. After the gases were removed from the cartridge by suction with a peristaltic pump, the flow-rate was set at 0.48 cm^3/sec with a stopcock connected to the Tenax-GC test cartridge. 4 μl of a standard in acetone containing 25 ng per component was then injected. Additional details concerning this apparatus are available elsewhere[5]. After 1 l of water has passed through the sampling cartridge, residual water was removed using a two-step centrifugation/vacuum desiccation procedure[5].

The cartridges were desorbed in the apparatus described earlier[5], and the analytes thereby transferred to the capillary column interface system described by Pankow *et al.*[6]. Prior to the desorption of this interface to a capillary column at −30°C, 26.6 ng of the internal standard 2-bromo-*m*-xylene in 2 μl of acetone were added by syringe to the interface Tenax-GC cartridge (capacity 0.12 g, 35–60 mesh).

GC–MS–DS analyses

The 30 m × 0.25 mm I.D. SE-54 fused silica capillary column was obtained from J & W Scientific (Rancho Cordova, CA, U.S.A.). The inlet end of the column was connected to the capillary interface, and the exit end was run through a capillary transfer line directly to within 0.5 mm of the ion source of a Finnigan 4000 gas chromatograph–mass spectrometer–data system (GC–MS–DS). The transfer line, source, and MS manifold temperatures were maintained at 220, 250, and 100°C, respectively. The helium carrier gas linear velocity was 35 cm/sec. After the desorption of the interface, the GC oven temperature was raised ballistically to 50°C, then programmed at 10°/min to 220°C. MS data acquisition was begun at 50°C. Quantitation for the compounds *o*-dichlorobenzene, 1,2,4-trichlorobenzene, naphthalene, and hexachloro-1,3-butadiene was carried out based on the ion peak areas for the m/z values 146, 180, 128, and 225, respectively, the internal standard (2-bromo-*m*-xylene)

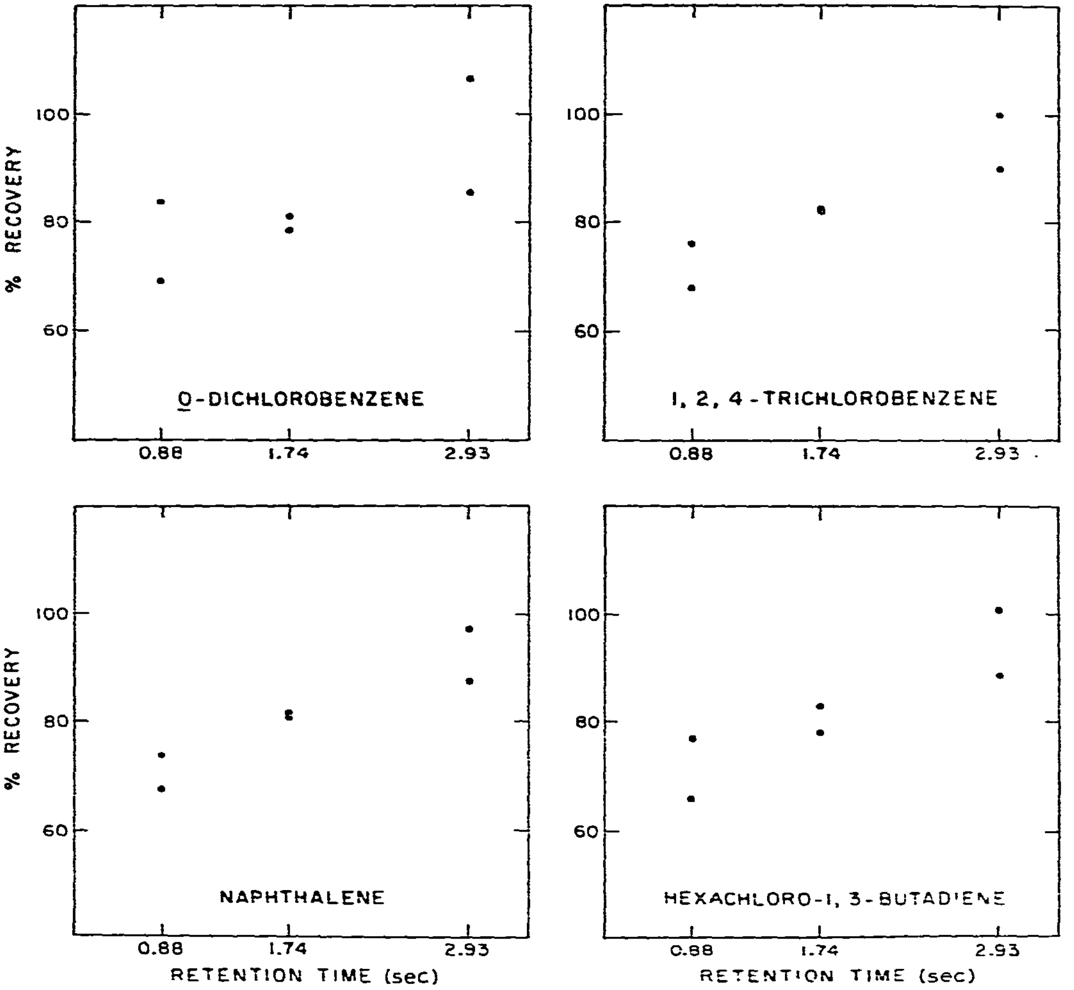

Fig. 2. Per cent recovery ($R \times 100$) as a function of retention time, τ, for constant $v_s = 1.28$ cm/sec. Experiments carried out with cartridge types 1, 2, and 3.

ion peak area at m/z 105, and the relative response factors obtained in a prior standard run.

RESULTS AND DISCUSSION

The recoveries obtained with each cartridge type are plotted as a function of τ with v_s constant (Fig. 2) and as a function of v_s with τ constant (Fig. 3). The fact that R should increase with τ is expected. It is important, however, that large effects on R were observed in the range $0.88 \leqslant \tau \leqslant 2.93$; small effects on R would not be consistent with our earlier interpretation of the experimental data plotted in Fig. 1 for which $0.92 \leqslant \tau \leqslant 7.38$ and $0.39 \leqslant v_s \leqslant 3.14$. That varying v_s in the range $0.70 \leqslant v_s \leqslant 2.00$ should also have a large effect provides additional strong evidence for this

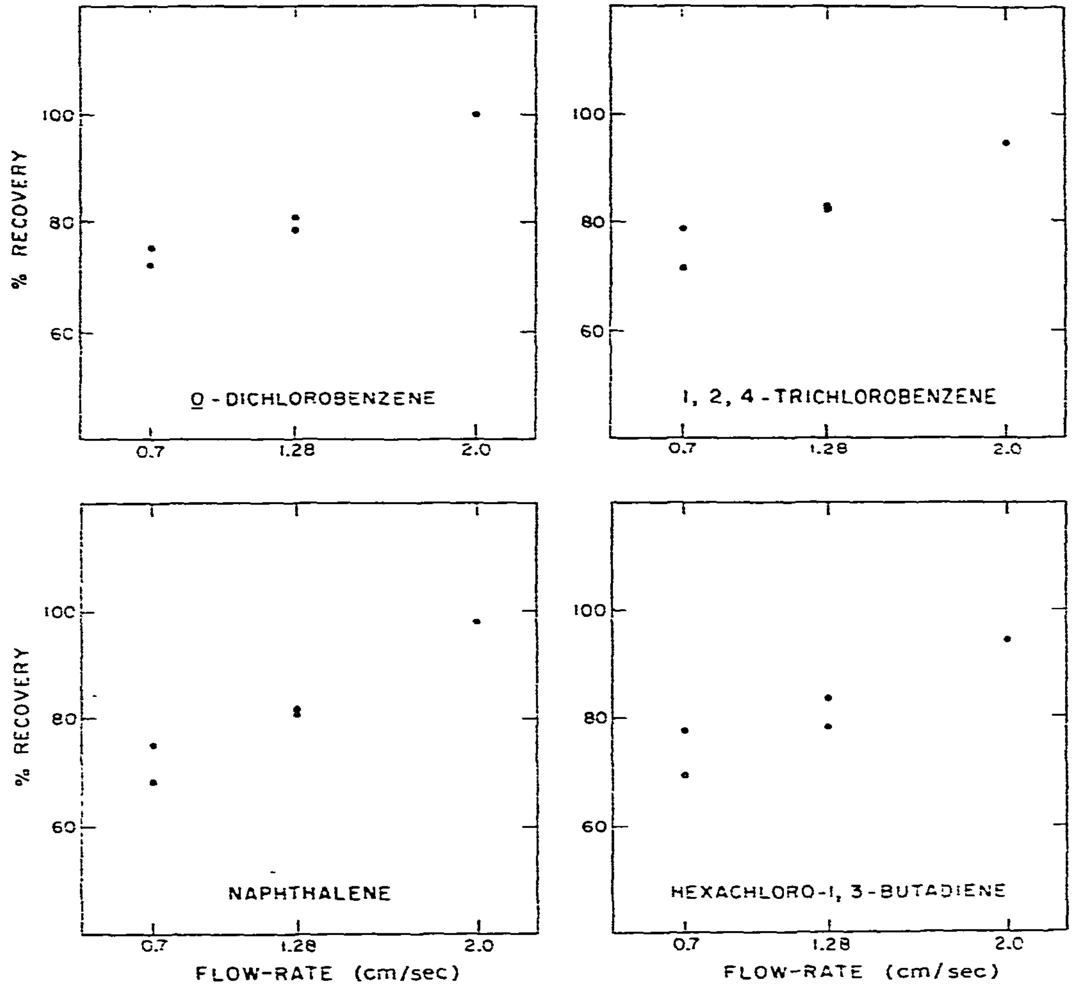

Fig. 3. Per cent recovery ($R \times 100$) as a function of superficial velocity, $v_s = V/A$, for constant $\tau = 1.74$ sec. Experiments carried out with cartridge types 4, 2, and 5.

interpretation, particularly since the increase in R with increasing v_s occurred with cartridges containing the same amount of Tenax-GC (types 4, 2, and 5). All of these results lead to the conclusion that film diffusion is indeed controlling in beds of Tenax-GC for the flow-rates studied. They also validate the use of eqn. 6 for calculating R values.

There are, however, several difficulties in the *a priori* application of eqn. 6 for short beds of Tenax-GC. They are: (1) the parameters D, p, r, and δ may be only poorly known; (2) uncertainty in the actual particle surface area for diffusion (*i.e.*, $2\pi r^2$ *vs.* $4\pi r^2$, ref. 15); (3) particle non-sphericity; and (4) polydispersity of the particles. The experimental data presented in Figs. 2 and 3, however, provide a means of estimating the *effective* value of the group $3D(1 - p)/2r\delta$ for Tenax-GC (35–60 mesh) cartridges packed to a density of roughly 0.16 g/cm^3. Fig. 4 presents plots of this

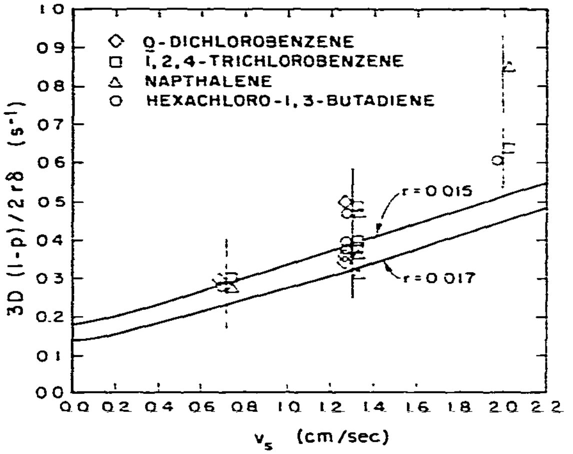

Fig. 4. Experimental determinations of the effective value of the group $3D(1 - p)/2r\delta$(sec^{-1}). Experimental points calculated as $-V \ln (1 - \bar{R})/AL$. $\bar{R}$ = Average R obtained for replicate experiments with Tenax-GC (35–60 mesh) packed to a density of 0.16 g/cm^3. Theoretical curves calculated by means of eqn. 6 for two values of r with $D = 8 \times 10^{-6}$ cm^2/sec, $p = 0.38$, $V = 0.48$ cm^3/sec, and δ given by eqn. 2.

group, calculated as $-V \ln (1 - \bar{R})/AL$, as a function of v_s for the four compounds studied. $\bar{R}$ represents the average R obtained for the duplicate experiments carried out for each type of cartridge. (Only one experiment was carried out at $v_s = 2.0$). The precision between compounds at $v_s = 0.70$ indicates that differences in the diffusion coefficients are small. The data indicate an upturn in the value of this group as v_s is increased, that is, as δ is decreased. The group $3D(1 - p)/2r\delta$ has also been calculated by assuming that δ is given by eqn. 2 with $D = 8 \times 10^{-6}$ cm^2/sec and $p = 0.38$. An r value of 0.015 cm gives a better fit than 0.017 cm, though it still underestimates the experimental data at high v_s values.

The spread in the data at $v_s = 1.28$ and $v_s = 2.0$ is due to the fact that for some of the data points, R was ≈ 1. In such cases, the quantity $V \ln (1 - R)/AL$ is difficult to estimate accurately. Thus, the issue of whether or not curve A actually underestimates $3D(1 - p)/2r\delta$ at $v_s = 2.0$ is somewhat uncertain, and we conclude that the equation for curve A

$$3D(1 - p)/2r\delta = 0.165\,(1 + 1.05\,v_s) \tag{7}$$

will allow conservative estimates of R to be made for cartridges of Tenax-GC (35–60 mesh) (packing density 0.16 g/cm^3). On this basis, R may be calculated as a function of V for any cartridge volume, V_c ($V_c = AL$), by eqn. 8:

$$R = 1 - e^{0.165(1 + 1.05V/A)V_c/V} \tag{8}$$

Similarly, the L value required to yield a given R value may be calculated by eqn. 9:

$$L = \frac{\dfrac{-\ln (1 - R)}{0.165} \cdot \dfrac{V_c}{V}}{1.05} \tag{9}$$

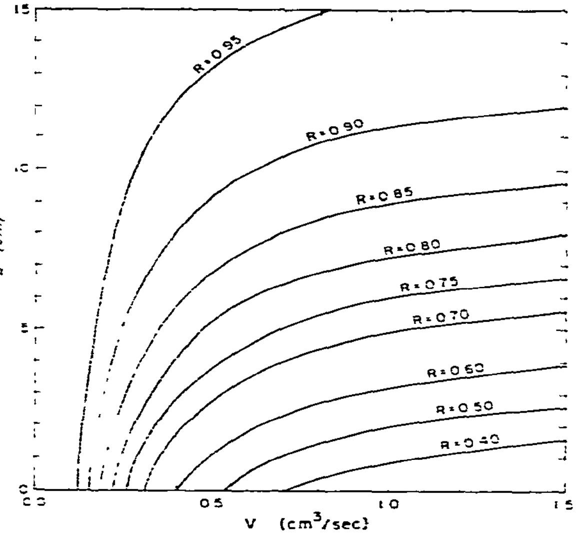

Fig. 5. The value of L (cm) required to obtain a given R value plotted as a function of the volume flow-rate, V (cm³/sec). Calculations based on eqn. 9 for $V_c = 2.2$ cm³.

Some caution must be exercised in the use of eqns. 8 and 9. Both are based on eqn. 2 which will not be valid for unlimited values of v_s. Also, eqn. 8 illustrates that zero is the only value of R compatible with a zero value of V_c. Therefore, calculating the required L value (eqn. 9) for a non-zero R value when V_c is zero would be meaningless. Finally, very small L values of the order of the r will not be meaningful since "typical" flow characteristics will not have a chance to develop. This is not a problem, however, since very small L values imply unrealistic A values.

A particularly useful application of eqn. 9 is that it provides a means of calculating curves of constant R as a function of L and V for a constant V_c value. Given desired values of V_c and R, the importance of analysis time (*i.e.*, V) may be weighed against increasing L values and the concomitant increasing pressure differentials required during sampling. Fig. 5 provides examples of such curves for a cartridge with the same V_c as the type 2 cartridges used in this study. This figure ties together several important phenomena observed with Tenax-GC cartridges. For constant cartridge dimensions (constant L), the recovery becomes constant at large V because δ becomes inversely proportional to τ (see eqn. 2). At a constant flow-rate and V_c, increasing L increases R because δ is decreasing but τ is remaining constant (as in cartridge types 4, 2, and 5).

The maximum value for v_s in Fig. 5 occurs in the upper right hand corner where $v_s = 10.2$ cm/sec. According to eqn. 2, for $r = 0.015$ cm, δ would then be only $\approx 3 \times 10^{-4}$ cm. This is substantially less than the typically observed δ value of 10^{-3}–10^{-2} cm[14]. Whether or not such a small δ value is meaningful for beds of Tenax-GC (35–60 mesh) is not known. (Certainly there will be some lower bound on the effective value of δ due to stagnation in pores and crevices.) Therefore, the greatest reliability may be assigned to the curves and portions of curves not located in the upper right quadrant of Fig. 5.

With a V_c of 2.2 cm³, the lack of reliability of the curves in the upper right

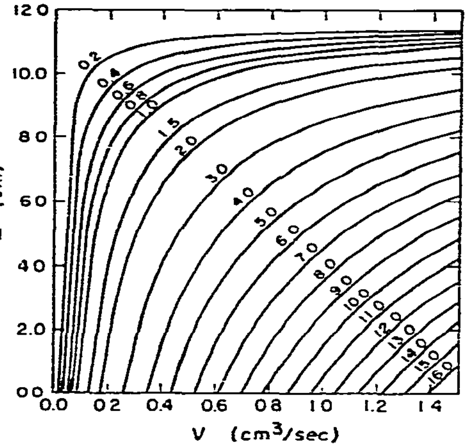

Fig. 6. The value of L (cm) required to obtain an R value of 0.85 plotted as a function of the volume flow-rate, V (cm^3/sec), for a range of V_c (cm^3) values. Calculations based on eqn. 9.

quadrant of Fig. 5 is not a problem since the use of long, narrow cartridges at high flow-rates is not attractive. Such cartridges would be cumbersome, and the pressure differentials required to operate them at high V values would be inconvenient. Moreover, reasonable R values may be obtained at lower L and V values. Since v_s will tend to increase as V_c decreases, however, greater care must be exercised in interpreting plots like Fig. 5 prepared for smaller V_c.

Fig. 6 demonstrates another application of eqn. 9. In this case, a constant, reasonably high, but not too demanding R value of 0.85 has been chosen. Now the advantages of decreasing analysis time by increasing V may be weighed against the need to use cartridge beds of increasing L for a variety of V_c values. As with Fig. 5, the upper right quadrant of this plot represents very large v_s values and perhaps unrealistically small δ values. For example, for $V_c = 0.2$ cm^3 and $V = 1.5$ cm^3/sec, according to eqn. 2 with $r = 0.015$ cm, δ is extremely small at only $3.4 \cdot 10^{-5}$ cm. However, the desirability and practicality of using long, narrow, low volume cartridges at high flow-rates is so small that unreliability in the upper right quadrant is not a problem. Figures similar to Fig. 6 but with decreasing R values will have an increasing level of reliability in the upper right quadrant.

CONCLUSIONS

Strong evidence has been obtained which indicates that the retention of aqueous, non-polar organics on Tenax-GC is film diffusion controlled. Thus, the early "breakthrough" which has been experienced (though often not reported) by some workers investigating aqueous sampling with Tenax-GC was possibly the result of poor *transport* and not the result of poor *retention*. A basic assumption in our development of the equations relating R to various experimental parameters has been that the Tenax-GC particles will act as a perfect sink for the analyte compounds. Clearly, this will be valid only: (1) when the analytes are not very water soluble; (2) when they are present at relatively "low" concentrations; and (3) when background organic contaminants are also "low". The last two requirements are needed in order that the sorption capacity of the Tenax-GC is not exceeded. These two criteria will be met by unpolluted lake, river, and sea water, as well as by rain and snow.

In terms of the analyte concentrations, the exact meaning of "low" will be compound-dependent. Since good recoveries were obtained at the total loading level of 1 μg for the compounds *p*-dichlorobenzene, hexachloro-1,3-butadiene, and 2-chloronaphthalene[5], levels such as 1 μg/l may be considered "low". Considering the tremendous sensitivity of the method, however, high analyte levels may be easily handled using smaller samples. What is meant by "low" concentrations of background organics such as solvents (often present at ppm levels in waste effluents and contaminated waters) and naturally occurring humic materials is presently under study in our laboratory.

For the compounds studied in this work, the perfect sink assumption and the invoking of film diffusion controlled transport have provided a theoretical basis for understanding and predicting the efficiency with which beds of Tenax-GC retain certain organic compounds. While this work was limited to 35–60 mesh Tenax-GC an examination of the various recovery equations presented here demonstrates that the use of particles in the 60–80 mesh range will provide higher recoveries at all v_s values. However, the higher permeability to flow possessed by a bed of 35–60 mesh Tenax-GC remains attractive and, as demonstrated in Fig. 5, conditions may be found which give high recoveries for this mesh range.

SYMBOLS

A	bed cross-sectional area (cm^2)
$c_b(x)$	concentration (mass per cm^3) of analyte in bulk liquid in void volume at position x in the bed
c_e	concentration (mass per cm^3) of analyte in effluent from bed
c_i	concentration (mass per cm^3) of analyte in influent to bed
$c_s(x)$	concentration (mass per cm^3) of analyte in liquid at surface of the particles at position x in the bed
δ	hypothetical thickness of stagnant boundary layer
D	diffusion coefficient (cm^2/sec)
F	flux (mass per cm$^2 \cdot$ sec)
L	length (cm) of bed
n	number of theoretical plates
p	bed porosity
r	radius (cm) of bed particle
R	fractional recovery
$\bar{R}$	fractional recovery for duplicate runs
τ	retention time (sec) of liquid in bed
V	volume flow-rate (cm^3/sec) through bed
V_c	volume (cm^3) of cartridge bed
V_R	retention volume (cm^3)
v_s	superficial velocity (V/A, cm/sec)
x	coordinate coaxial with bed
z	number of particles per cm of the bed [$3(1 - p)\,A/4\pi r^3$, cm^{-1}]

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