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Note

Theoretical plate measurements and collection efficiencies for high-volume air samplers using polyurethane foam

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Solid adsorbent cartridges are widely used to collect organic vapors, and an important step in sampling methods development consists of determining their ability to collect vapors without breakthrough loss. Under conditions where the adsorbent capacity is not exceeded, solute penetration through an adsorbent bed follows well-known chromatographic relationships. The collection efficiency depends on the retention or breakthrough volume (V_R or V_B) and the number of theoretical plates (N) in the bed¹⁻⁷. These parameters are usually obtained from elution or frontal gas chromatographic (GC) experiments. A large number of V_R and V_B measurements have been made for volatile substances (e.g., solvent vapors) sampled with polymeric adsorbents, and N are known for small cartridges containing a few hundred milligrams adsorbent. Examples of these studies are given in refs. 2-6.

Chromatographic experiments to define the collection efficiency of high-volume (hi-vol) samplers are less common. Hi-vol systems use collection traps containing gram quantities of adsorbent, and V_R or V_B of high-molecular-weight organic compounds are typically hundreds to thousands of cubic meters. Conventional GC experiments in which the column effluent is continuously monitored with a detector to determine breakthrough are thus not feasible. Instead, we have used a "hi-vol gas chromatograph" to measure V_R and V_B of heavy organic compounds at ambient temperatures⁷⁻⁹. In this technique, vapors are introduced in an elution or frontal mode to a column containing thin sections of adsorbent, polyurethane foam for our studies. Analysis of individual polyurethane foam slices provides a detailed profile of vapor penetration and chromatographic parameters can be determined from the position and shape of the bands or fronts. In a recent paper⁷ we described the calculation of V_B and N from polycyclic aromatic hydrocarbon (PAH) fronts and used these parameters to predict PAH collection efficiencies at different air volumes. The purpose of this article is to provide more information on N for polyurethane foam hi-vol samplers at different flow-rates and to extend collection efficiency estimates to some organochlorines for which V_B have been previously determined⁸.

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EXPERIMENTAL

The apparatus and methods used in elution and frontal chromatographic studies have been described elsewhere⁷⁻⁹ and will only be summarized here. A column was packed with 15 polyurethane foam slices, each 7.6–7.8 cm diameter \times 1.0 cm thick (density = 0.022 g/cm³). Laboratory air was pulled through a large polyurethane foam pre-filter to remove contaminants and then through the collection column. The flow-rate for elution experiments was varied between 0.15–0.8 m³/min, whereas all frontal experiments were carried out at 0.5–0.6 m³/min. Microgram quantities of organochlorines or PAH were introduced by spiking the first polyurethane foam slice (elution mode) or by bleeding vapors into the air stream from a coated glass-beads saturator column (frontal mode). After sampling, residues on each polyurethane foam slice were solvent extracted and determined by GC using electron-capture (for organochlorines) or flame ionization (for PAHs) detection.

The following organochlorines and PAHs were used: 3,3'-dichlorobiphenyl (3,3'-DCB), 2',3,4-trichlorobiphenyl (2',3,4-TCB), 2,4',5-trichlorobiphenyl (2,4',5-TCB), hexachlorobenzene (HCB), fluorene (FLE), phenanthrene (PH), anthracene (AN), and pyrene (PY). Chlorobiphenyls and HCB were obtained from Analabs, Inc. and the U.S. Environmental Protection Agency Pesticides and Industrial Chemicals Repository, respectively. PAHs were analytical reagent grade. All solvents were pesticide analytical quality.

RESULTS AND DISCUSSION

Examples of elution and frontal vapor profiles within the polyurethane foam bed and constructions used to calculate N are shown in Fig. 1. N dropped from 2.1 plates/cm polyurethane foam at 0.15 m³/min to 0.8 plates/cm at 0.8 m³/min (Fig. 2). Flow-rate was varied only for the elution experiments. However, between 0.4–0.55 m³/min N determined from elution and frontal experiments agreed excellently, suggesting that the flow-rate dependence in Fig. 2 applies to frontal chromatography as well.

Theoretical plate measurements for the polyurethane foam hi-vol sampler can be compared with those for low volume (lo-vol) cartridges. Linear air velocities corresponding to the flow-rates in Fig. 2 ranged from 3.3–18 m/min. Brown and Purnell² and Clark *et al.*⁴ reported N for 4.5 mm diameter \times 7.5 cm long cartridges containing 130 mg Tenax. When acetone, dichloromethane, propylamine, and benzene were sampled at 50 ml/min (linear air velocity = 0.31 m/min), N /cm ranged from 4.5–8.5. Raising the flow-rate to 600 ml/min (linear air velocity = 3.8 m/min) decreased N /cm to 1.1–2.7². The latter values are remarkably close to the 2.1 plates/cm obtained with the hi-vol polyurethane foam sampler at linear air velocity = 3.3 m/min.

Our hi-vol collector for field work uses two polyurethane foam plugs, each 7.6–7.8 cm diameter \times 7.5 cm thick, and operates at 0.4–0.6 m³/min¹⁰⁻¹². At this flow-rate the average N is approximately one plate/cm polyurethane foam, or 7.5 plates for a single field sampling plug.

The penetration depths of vapor front midpoints for three organochlorines and four PAHs were plotted vs. air volume, and V_B at 20°C were obtained for a 7.6–7.8 cm diameter \times 7.5 cm thick polyurethane foam plug (Table I)^{7,8}. In a pre-

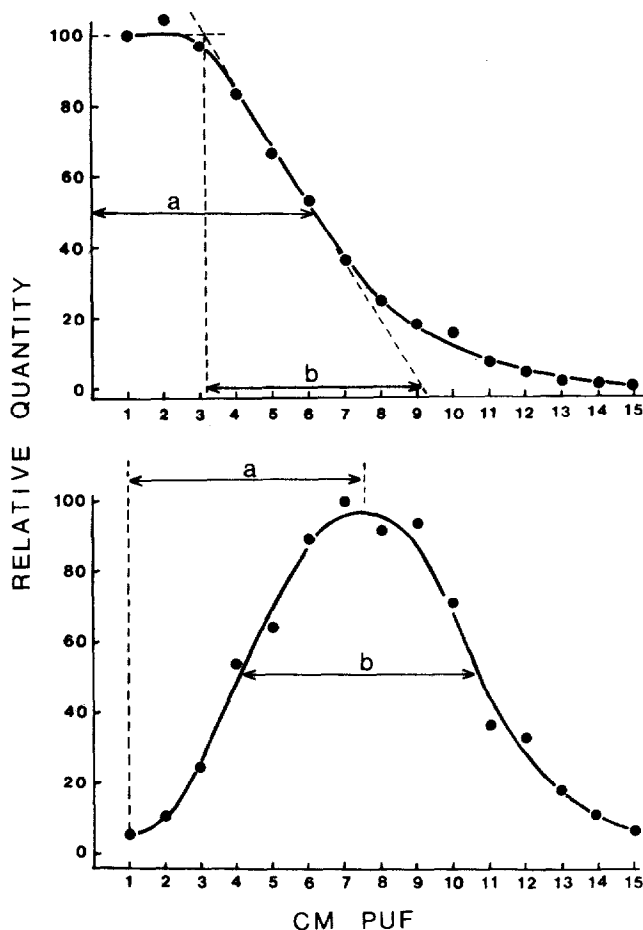


Fig. 1. Top: PH front, 648 m³, 0.55 m³/min, $N = 2\pi(a/b)^2$. Bottom: 3,3'-DCB elution band, 600 m³, 0.5 m³/min, $N = 5.5(a/b)^2$. The first cm polyurethane foam (PUF) was spiked in the elution experiments, so distance a was measured from this point.

vious paper⁷ we showed that $\log V_B$ for the PAHs was inversely related to \log vapor pressure, and that the correlation was improved if the vapor pressure of the sub-cooled liquid (P_L) rather than the solid (P_S) was used. The same is true for the organochlorines. In Fig. 3 $\log V_B$ for two chlorobiphenyls and HCB are plotted against P_L and P_S . These physical constants are given in Table II. The P_L values for the chlorobiphenyls were determined by a capillary GC method¹³ and the P_S value of HCB is the average of several literature values¹⁴⁻¹⁶. P_L and P_S were interconverted using

$$\ln P_L/P_S = 6.8 (T_m - T)/T \quad (1)$$

where T_m and T are the absolute melting point and ambient temperatures and 6.8 is a constant related to the entropy of fusion¹⁷. The difference between the two vapor

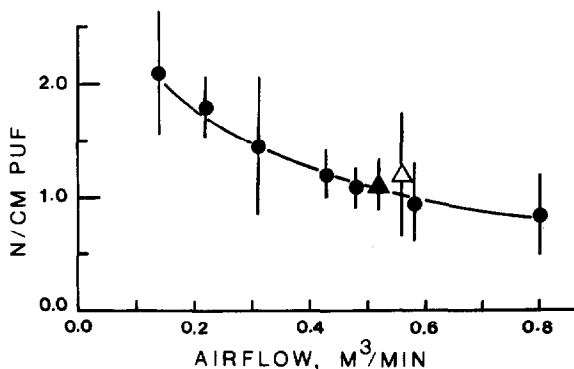


Fig. 2. Average $N \pm$ standard deviation at different flow-rates. (●) Elution experiments (3–16 at each flow-rate) using 3,3'-DCB, 2',3,4-TCB, and 2,4',5-TCB; (△) 13 frontal experiments using HCB, 3,3'-DCB, and 2,4',5-TCB; (▲) 9 frontal experiments using FLE, PH, and AN. PUF = polyurethane foam.

pressures is large for compounds with high melting points. P_L and P_S are close for 3,3'-DCB (m.p. 29°C), but P_L is 130 times P_S for HCB (m.p. 230°C).

Log V_B correlated well with log P_L but not with log P_S (Fig. 3). The compound most noticeably out of line was HCB, with a V_B far too low relative to its solid phase volatility. When a similar plot was made for PAH⁷, V_B for AN (m.p. 216°C) showed the same behavior. Thus, the ability of solid adsorbents to collect vapors of high-melting-point compounds cannot be estimated from P_S ; P_L should be used. In general, partitioning of a solute is better correlated with liquid rather than solid physical properties because of the large effect of the crystal lattice energy on such properties¹⁸. Bioaccumulation of organic compounds is best correlated with the liquid-phase solubility¹⁹, and the partitioning of non-polar compounds in gas-liquid chromatography is governed by P_L rather than P_S ¹³.

Sampling volumes (V_S) corresponding to designated collection efficiencies can be estimated from solute V_R and N using a nomograph constructed by Senum¹. We

TABLE I

BREAKTHROUGH VOLUMES (V_B) AT 20°C FOR CHLORINATED HYDROCARBONS AND PAHs, AND SAMPLING VOLUMES (V_S) CORRESPONDING TO DESIGNATED COLLECTION EFFICIENCIES

Polyurethane foam column 7.6–7.8 cm diameter \times 7.5 cm thick, $N = 7.5$.

Compound	V_B (m^3)	V_S at collection efficiency	
		90%	95%
HCB	125	103	78
3,3'-DCB	720	590	446
2,4',5-TCB	1440	1180	893
FLE	120	100	77
PH	800	660	500
AN	1100	920	690
PY	10,000	8200	6200

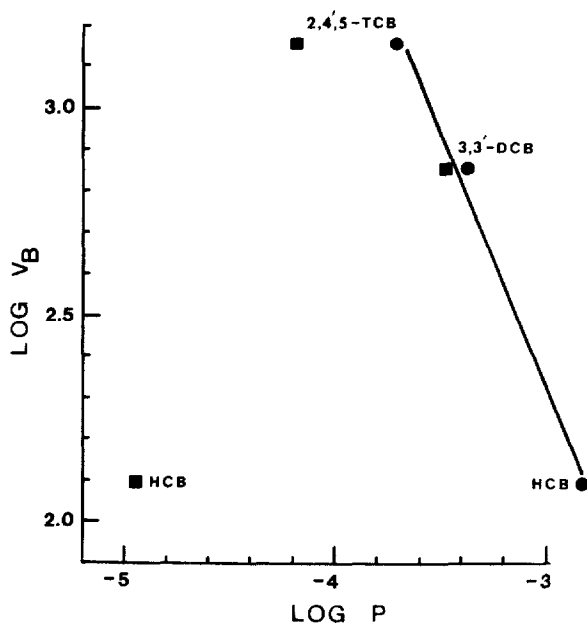


Fig. 3. Variations in organochlorines $\log V_B$ with (■) $\log P_S$ and (●) $\log P_L$.

have done this for the compounds in Table I collected on a single polyurethane foam plug ($N = 7.5$) at 20°C . In these calculations, the V_B in Table I were used instead of V_R . The two chromatographic parameters are equivalent if V_B is defined by the vapor front midpoint²⁰.

Our hi-vol sampler draws about 600 m^3 air through a glass fiber filter and two polyurethane foam plugs in 24 h. From the V_S in Table I, the 3- and 4-ring PAHs and the two chlorobiphenyls will be quantitatively collected at 20°C whereas HCB and FLE will not. Field studies have also demonstrated the ability of polyurethane foam to collect the 3-4 ring PAH^{12,21} but not HCB^{10,11}. In an actual sampling situation, temperatures will differ from 20°C and will vary over 24 h. Vapor pressures of many high-molecular-weight organics increase by a factor of about 1.7-1.9 with a 5°C rise in temperature, so for sampling at temperatures other than 20°C , the parameters in Table I should be adjusted accordingly.

TABLE II

PHYSICAL PROPERTIES OF THE ORGANOCHLORINES USED IN V_B DETERMINATIONS

Compound	m.p. ($^\circ\text{C}$)	Vapor pressure at 20°C (Torr)	
		P_S	P_L
3,3'-DCB	29	$3.3 \cdot 10^{-4}$	$4.1 \cdot 10^{-4}$
2,4',5'-TCB	67	$6.2 \cdot 10^{-5}$	$1.8 \cdot 10^{-4}$
HCB	230	$1.1 \cdot 10^{-5}$	$1.5 \cdot 10^{-3}$

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