

Table I. Determination of Sulfate in Rainwater Samples

sample no.	mg/L sulfate					
	FI	s	%s	IC	Δ	% Δ
1	0.78	0.08	10.3	0.91	-0.13	-14.3
2	3.75	0.08	2.1	3.90	-0.15	-3.8
3	3.50	0.02	0.6	3.52	-0.02	-0.6
4	2.60	0.04	1.5	2.51	+0.09	+3.6
5	1.75	0.05	2.9	1.67	+0.08	+4.8
6	0.82	0.01	1.2	0.83	-0.01	-1.2
6A ^a	0.80	0.03	3.8			
7	1.23	0.14	11.4	1.31	-0.08	-6.1
7A ^a	1.24	0.04	3.2			
8	0.67	0.03	4.5	0.69	-0.02	-2.9
9	2.23	0.07	3.1	2.37	-0.15	-6.3

^a Samples 6A and 7A were spiked with an additional 1.0 mg/L calcium. Standard deviations are based on $N = 3$ except for sample 7A where $N = 6$.

Many cations interfere with the determination of sulfates using MTB (5). Sample pretreatment with a cation exchange resin in the H^+ form will eliminate this interference. Rain samples collected in Florida typically contain 0.2 mg/L calcium and 0.2 mg/L magnesium. The addition of 1.0 mg/L calcium to two different rain samples did not alter results for sulfate by the FI method as can be seen from results presented in Table I.

The detection limit for the system was not extensively evaluated. Base line variability is caused by commutation of the injector which momentarily blocks the sample carrier stream. This causes momentary flow upset within the system and results in changes in MTB reagent and sodium hydroxide concentrations. The effect on the FI absorbance profile is shown in Figure 4 when a sample of deionized water is injected into the system. The two damping coils located immediately before and after the injector (Figure 1) function to dampen the shock of injector commutation; however, a more appropriate solution to the problem would be to include an injector

bypass (14). Maximum base line upset corresponds to no more than 0.005 ΔA or 0.13 mg/L sulfate. The mean ΔA and standard deviation observed for 0.1 mg/L and 0.25 mg/L sulfate standards during calibration was 0.0031 ± 0.0007 and 0.0077 ± 0.0010 , respectively. Expanded scale FI absorbance profiles for 0.5, 0.25, and 0.10 mg/L sulfate standards are also included in Figure 4. These clearly show the applicability of the technique to samples with low sulfate concentrations. Typical concentrations of sulfate in rainwater are seldom less than 0.5 mg/L.

The method is well suited for reasonably rapid, accurate, and precise measurement of up to 6.0 mg/L sulfate in rainwater. Higher concentrations can be determined utilizing sample dilution. System startup time is minimal and a stable base line can be achieved within 10 min.

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Frontal Movement of Hexachlorobenzene and Polychlorinated Biphenyl Vapors through Polyurethane Foam

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Frontal chromatographic movement of hexachlorobenzene (HCB) and di- and trichlorobiphenyl (DCB and TCB) vapors through a polyurethane foam bed was examined under high volume airflow. The chlorinated compounds were continuously bled from a coated glass bead reservoir into the airstream and swept onto a column containing 15.76 cm diameter \times 1 cm thick foam plugs. Each compound moved through the bed as a front. Penetration depths of the fronts depended on the ambient temperature and volatility of the compounds and were linearly related to total air volume. Breakthrough volumes for the 15-cm foam column at 20 °C were 250 m³ for HCB, 1330 m³ for 3,3'-DCB, and 2880 m³ for 2,5,4'-TCB. Breakthrough volumes for the chlorobiphenyl isomers agreed well with retention volumes derived from previous high volume elution experiments.

Table I. Retention and Breakthrough Volumes for a 15-cm PPF Column

compd	V_R , m ³ air	V_B , m ³ air
	elution expt (12) 23-26 °C	frontal expt (this work) 20 °C
HCB		250
3,3'-DCB	1250	1330
2,5,4'-TCB	2700	2880

Use of porous polyurethane foam (PPF) as an adsorbent for high volume air sampling has proven advantageous due to its ease of handling and cleanup and its ability to capture many different organic compounds. These properties have resulted in extensive use of PPF for collecting airborne pol-

lutants such as chlorinated pesticides (1-4), polychlorinated biphenyls (PCB) (1, 3, 5-9), phthalate esters (7-9), polychlorinated naphthalenes (10), and herbicides (11). However, the collection efficiency of PPF is dependent on the pollutant vapor pressure as well as on the total air volume sampled. Collection efficiency in the field is determined by observing the amount of chlorinated hydrocarbons (CHC) on a backup adsorbent trap. For a given compound, increasing penetration to the backup trap is found at higher air volumes, indicating a frontal chromatographic movement of vapors through the adsorbent bed. For 12-48 h sampling times (300-1600 m³ air), the degree of breakthrough is greater for low molecular weight PCB (Aroclor 1016) than for the less volatile Aroclor 1254, while hexachlorobenzene (HCB) is inadequately retained by PPF (3).

Simon and Bidleman (12) demonstrated that a PPF column performs as a chromatographic system. In their work a single application or "slug" of sample was introduced at the head of a 15 cm long × 7.6 cm diameter PPF column and eluted with prefiltered air. Analysis of the 15 1 cm thick PPF slices revealed that (a) PCB isomers moved through the column as bands, (b) movement of Aroclor 1016 components through a PPF bed paralleled their order of elution from a GC column, and (c) penetration of an isomer band maximum was linearly related to total air volume.

The limitation of this experiment lies in the fact that it does not adequately reflect field sampling conditions. In the field, sample is continuously introduced and subsequently moved through the column as a front. This work is an extension of the experiments done by Simon and Bidleman, but conditions more approximate those in the field by continuous introduction of sample vapors. Although studies of frontal movement of vapors through adsorbent columns have been done at low total air volumes (13, 14), this study is the first demonstration of high volume frontal chromatography. This work is aimed at developing a method for predicting the movement of the more volatile CHC through PPF and the amount of PPF needed to prevent breakthrough.

EXPERIMENTAL SECTION

Solvents: reagent grade acetone; pesticide quality petroleum ether.

Compounds: 3,3'-dichlorobiphenyl (DCB) and 2,5,4'-trichlorobiphenyl, obtained from Analabs, North Haven, CT; hexachlorobenzene (HCB) obtained from the U.S. Environmental Protection Agency Pesticide Repository, Research Triangle Park, NC.

PPF Plug Preparation. Several sheets of 1 cm thick PPF, density = 0.022 g/cm³ (Olympic Products Corp., Greensboro, NC, product number 3014) were compressed between two plywood boards; the upper board contained a number of 8.3 cm diameter holes. A drill press with a hole saw attachment was used to cut plugs of 7.6 cm diameter × 1 cm thick (12). The plugs were rinsed with water, Soxhlet extracted for 24 h with acetone, followed by a 24-h extraction with petroleum ether, and dried in vacuo.

To ensure plugs of uniform flow characteristics it was necessary to measure the pressure drop across each individual plug under high volume air flow. Even plugs from adjacent areas of the stock foam sheet can exhibit different flow rates (4, 12). Plugs having similar flow resistances were arranged in sets of 15 and used for an experiment.

Procedure. The sampling apparatus (Figure 1) was similar to that used in previous elution experiments (12) with some adjustments made for frontal chromatographic operation. The sampling train consisted of a prefilter, a sample introduction/mixing chamber, and a PPF collection column. The prefilter consisted of two large PPF plugs, 30 cm diameter × 7.6 cm thick, which were necessary to remove interferences from ambient air. A thermometer was inserted behind the prefilter to monitor air stream temperatures during the run. All experiments took place in a thermostated room at 20 ± 2 °C, except for one 30 °C run.

Continuous sample introduction took place directly behind the

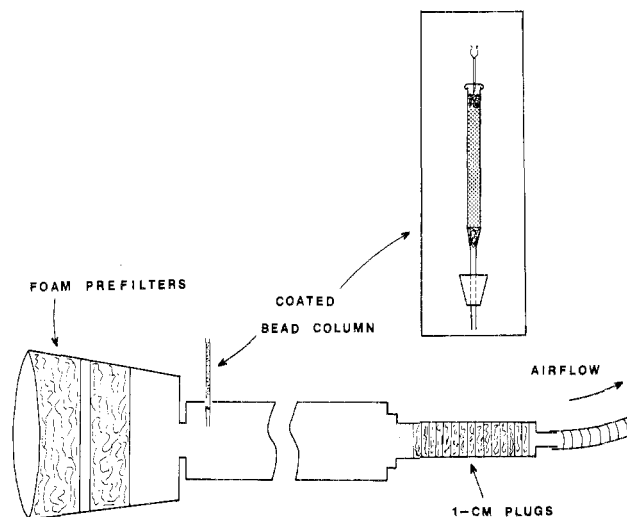


Figure 1. Apparatus used for studying frontal movement of CHC through PPF.

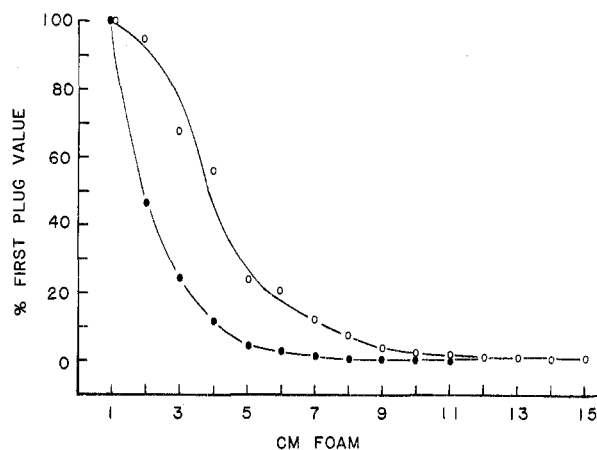


Figure 2. Frontal movement of (O) DCB and (●) TCB isomers through PPF, 400 m³ air.

prefilter. A pasteur pipet (Figure 1) was packed with glass beads which were coated with approximately 50 mg of a single compound of interest. Glass wool was used to hold the beads in place at either end of the pipet and the tip of the pipet was inserted into the mixing chamber. The slight vacuum in the system created by high volume air flow caused a stream of air to be drawn through the coated bead column, bleeding sample vapors into the mixing chamber. Air flow through the bead column was controlled by inserting 20-22 gauge hypodermic needles through a septum on the end of the pipet. A soap bubble meter was used to monitor the flow rate (6-25 mL/min) through the bead column.

The sample collector consisted of an aluminum barrel containing 15 loosely packed PPF plugs. A flexible hose connected the barrel to a high volume air pump (Rotron SL5P2, Rotron Corp., Woodstock, NY). The pressure drop across the system was measured with a Magnehelic gauge (Dwyer Instrument Co., Michigan City, IN). The relationship of this pressure drop and the flow rate was obtained by replacing the sampling train with an orifice calibrator containing variable resistance plates (15).

After the sample was taken, the plugs were Soxhlet extracted with petroleum ether. The extracts were concentrated on a flash evaporator, quantitatively transferred to Kuderna-Danish tubes, and shaken with 7% fuming H₂SO₄.

Extracts were analyzed on a 180 cm long × 0.4 cm i.d. glass column packed with 3% OV-225 on 100/120 mesh Supelcoport (Supelco Inc., Bellefonte, PA) using a Varian 3700 GC equipped with a ⁶³Ni electron capture detector. Analytical conditions were as follows: column temperature 190 °C, detector temperature 350 °C, injector temperature 220 °C, and carrier gas (N₂) flow 50 mL/min. The quantity of CHC compound found on individual PPF plugs was calculated and expressed either as the percentage

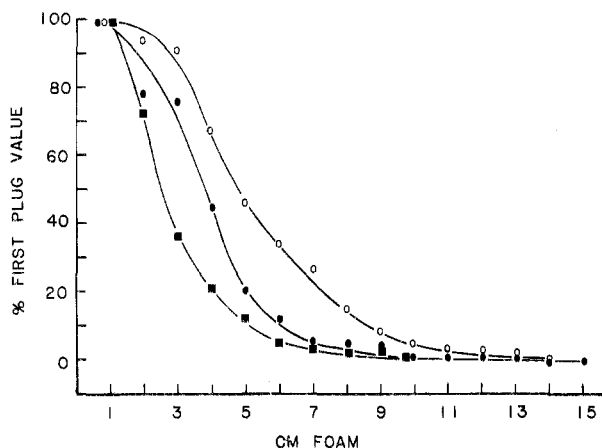


Figure 3. Frontal movement of TCB isomer through a PPF column at (■) 500, (●) 700, and (○) 900 m³ air.

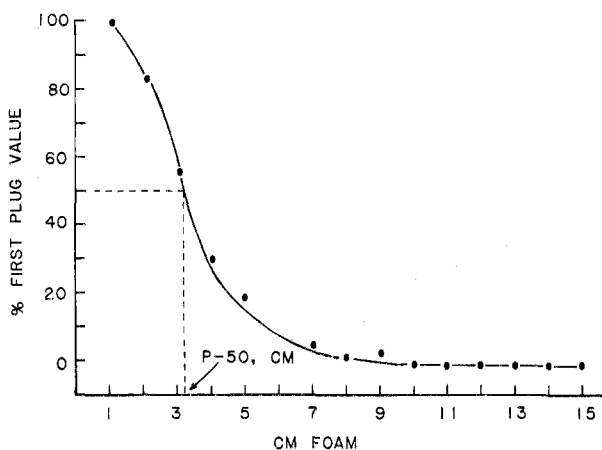


Figure 4. Frontal movement of hexachlorobenzene (HCB) through a PPF column, 50 m³ air. P-50 marks the point where the HCB concentration is 50% of that on the first foam plug.

of the first plug value (Figures 2-4) or cumulative percentage of the total recovered in all 15 plugs (Figure 7). Total CHC in the PPF trap ranged from 0.2 to 50 μg depending on the volatility of the compound, the airflow through the coated bead column, and the length of sampling.

RESULTS AND DISCUSSION

Frontal movement of hexachlorobenzene (HCB) and the two PCB isomers through a PPF bed is depicted in Figures 2-4. Simon and Bidleman (12) demonstrated that PCB isomers were eluted through a PPF column in order of decreasing volatility. In the frontal chromatographic experiment this is also the case, and Figure 2 shows that DCB has penetrated further into the column than the TCB for a given air volume. At 25 °C the vapor pressures of 3,3'-DCB and 3,4,2'-TCB are 2.0×10^{-4} and 8.0×10^{-5} mmHg, respectively (16). Preliminary studies have shown that the 2,5,4'-TCB isomer used for our frontal experiment has a vapor pressure very close to that of the 3,4,2'-TCB isomer, and the elution characteristics of these two isomers through PPF are similar (12).

As previously stated, vapor penetration through a PPF column is dependent on total air volume as well as volatility. Figure 3 demonstrates this for a TCB front at three different air volumes. As air volume is increased, the front penetrates further into the foam column.

The breakthrough volume, V_B , for a frontal experiment may be taken as the point at which the concentration of solute in the column effluent is half the concentration introduced to the column (13). This breakthrough volume should be identical with the retention volume, V_R , for an elution experiment carried out on the same column (17). The thickness

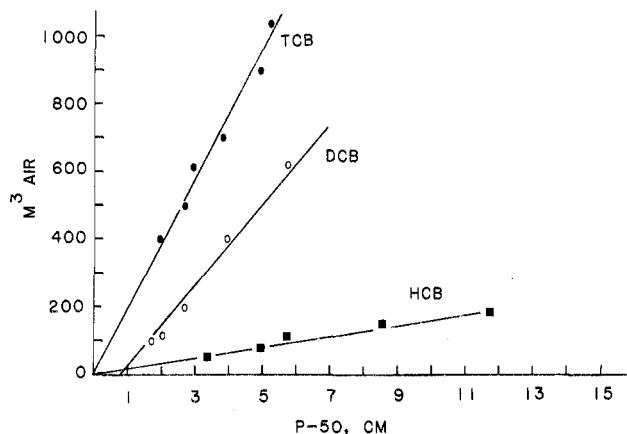


Figure 5. Linear movement of HCB, DCB, and TCB fronts through a PPF column with total air volume.

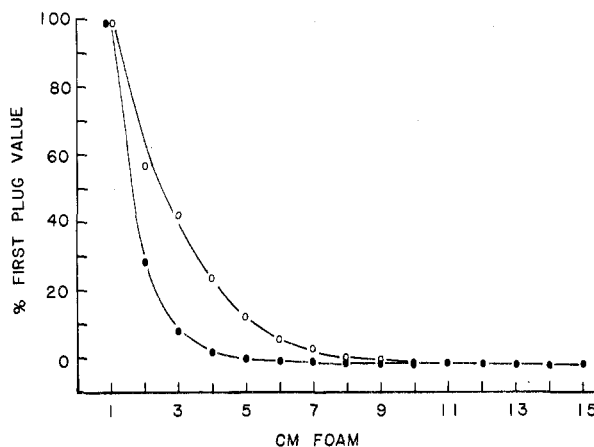


Figure 6. Effect of temperature on DCB frontal movement through a PPF column, 100 m³ air: (●) 20 °C (○) 30 °C.

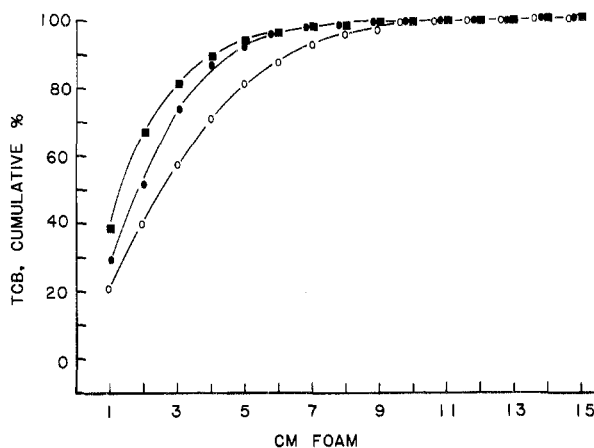


Figure 7. Cumulative percent of TCB retained by PPF at (■) 500, (●) 700, and (○) 900 m³ air. For n cm foam, cumulative percent = (μg of TCB on plugs 1 + 2 + ... + n)/(total μg of TCB on all 15 plugs).

of foam (P-50) corresponding to 50% breakthrough was obtained for each frontal experiment (Figure 4) and plotted against total air volume. As was the case for previous elution experiments (12), linear relationships between vapor penetration and total air volume were obtained (Figure 5). Extrapolation of these plots yielded V_B values for a 7.6 cm diameter \times 15 cm thick PPF column. The V_B values for DCB and TCB agreed excellently with V_R obtained in elution experiments (12) (Table I). The slightly greater V_B compared to V_R may be due to the fact that the frontal experiments were carried out at 20 °C, whereas the elution experiments were done at 23-26 °C. That temperature affects vapor penetration

can readily be seen in Figure 6, where DCB fronts at 20 and 30 °C are compared.

The problem of breakthrough of the more volatile CHC on PPF has plagued workers in the field. However, with these frontal experiments it is possible to predict that amount of PPF needed to prevent breakthrough at a given temperature and air volume. This is easily seen in Figure 7 where the results from Figure 3 have been replotted as the cumulative percent of TCB recovered at different air volumes. At 500 m³, 90% of the TCB is found within the first 4 cm of foam. At 900 m³, however, 7 cm of foam is required to retain 90% of the TCB. A series of these curves for compounds of differing volatilities would aid the selection of PPF bed volumes and sampling conditions.

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Characterization of the Basic Fraction of Marijuana Smoke by Capillary Gas Chromatography/Mass Spectrometry

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The basic fraction of Mexican marijuana smoke condensate was characterized by combined capillary gas chromatography/mass spectrometry. Enrichment of some trace components was accomplished with high-performance liquid chromatography, permitting tentative identification of nearly 300 nitrogen-containing sample components. A comparison with the basic fraction of tobacco smoke condensate, characterized by the same methodology, revealed that there are both qualitative and quantitative differences between the two condensate fractions.

An extensive use of marijuana together with the related question about its possible hazards to human health have increased scientific interests in these matters. Although much still remains to be learned about the social, pharmacological, and toxicological aspects of marijuana, a number of interesting observations were made over the last 2 decades. While many observed effects of this "drug" relate to its major psychoactive components, Δ^9 -tetrahydrocannabinol or other structurally related compounds (cannabinoids) present in the *Cannabis sativa* plant, it has been pointed out (1-3) that in certain cases

cannabinoids are not toxicologically and pharmacologically synonymous with marijuana. Obviously, other active, as yet unidentified, components must also be present.

The major way of marijuana use is by smoking, yet very little has been known about the chemical composition of the smoke. This situation can now be changed, since relatively standardized ways of smoke condensate preparation together with powerful multicomponent analytical methods (based on chromatographic principles) have become available in the research on tobacco carcinogenesis and related problems. With such methodology, it is quite feasible to separate and identify hundreds of marijuana plant and smoke components. In conjunction with biological testing, even trace components in very complex mixtures can be identified and potentially implicated in toxicity effects.

While glass capillary column gas chromatography and its combination with mass spectrometry are now extensively used in tobacco aroma and smoke research, employment of these techniques in marijuana-related investigations has been considerably less. Thus, smoke profile (4) and total condensate and hashish components (5) were recorded and further investigated, while a capillary gas chromatographic technique was also used for a forensic "fingerprinting" application (6). Maskarinec et al. (7) isolated acidic and phenolic components from marijuana smoke condensate and identified numerous components as their methyl and trimethylsilyl derivatives; certain differences between the samples of Mexican and Turkish marijuana were observed. Polycyclic aromatic hy-

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