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Note

Graphitized capillary columns for the determination of chlorinated compounds

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The determination of chlorinated organic compounds in environmental analysis is of great importance and there is a need for efficient gas chromatographic columns.

In this work we show that the analysis of complex mixtures containing chlorinated pesticides, polychlorinated biphenyls (PCBs) and other pollutants can be carried out by using graphitized capillary columns. These columns, introduced by Goretti and co-workers^{1,2}, have the interesting feature that according to the amount of stationary phase coated on the walls, they operate in gas-solid, gas-liquid and gas-liquid-solid chromatographic modes^{3,4}. This investigation was carried out with columns coated with PEG 20M and it is shown that selective columns can be obtained that give different performances suitable for particular applications.

EXPERIMENTAL

Pre-coating of glass capillary columns with graphitized carbon black was carried out according to the procedure developed by Goretti and Liberti⁵. A suspension of graphitized carbon black (Carbopak A; Supelco, Bellefonte, Pa., U.S.A.) was prepared by exposing to ultrasonic waves (20 kHz) for 40 min 65 mg of Carbopak A plus 7.5 mg of FFAP in a mixture of carbon tetrachloride (20 ml) and dichloromethane (6 ml). The suspension was made to flow through the column (two passages of 2 ml of suspension, in opposite directions). After washing with dichloromethane the column was dried and filled with a solution of PEG 20M at different concentrations in dichloromethane. The solvent was then removed by passing nitrogen through the column. The column was closed at both ends and conditioned overnight at a selected temperature.

All columns used had an I.D. of 0.24 mm, and the column lengths and the loadings of the stationary phase were as follows: column 1, 25 m, 0.04 mg/m; column 2, 31 m, 0.08 mg/m; column 3, 30 m, 0.16 mg/m; column 4, 15 m, 0.60 mg/m; and column 5, 70 m, 0.06 mg/m.

A DANI Model 3900 gas chromatograph with dual columns, equipped with an electron-capture and a flame-ionization detector, and connected to a Leeds and Northrup Speedomax Model XL681 recorder operating with 1 mV full-scale deflection was used.

RESULTS AND DISCUSSION

A mixture of fifteen chlorinated pesticides was subjected to gas chromatography on all columns under the same operating conditions at 160°. The values of the capacity ratio (k') and the retention volumes relative to dieldrin are given in Table I. The columns give the same elution sequence for most pesticides, with the exception of α -endosulfan and γ -chlordane, and endrin and p,p' -DDE. These compounds are eluted in the order given on columns 1 and 2, whereas the order is the reversed on other columns with higher loadings of stationary phase.

TABLE I

CAPACITY RATIOS (k') AND RETENTION VOLUMES (r) RELATIVE TO DIELDRIN AT 160°

No.	Pesticides	Column 1		Column 2		Column 3		Column 4	
		k'	r	k'	r	k'	r	k'	r
1	α -BHC	1.49	0.18	2.50	0.20	8.81	0.19	36.4	0.18
2	Heptachlor	1.70	0.21	2.63	0.21	9.02	0.20	40.0	0.20
3	Aldrin	1.81	0.22	2.85	0.23	9.80	0.21	42.1	0.21
4	γ -BHC	2.51	0.31	3.80	0.31	16.8	0.36	62.9	0.31
5	α -Endosulfan	5.41	0.66	7.92	0.65	31.2	0.66	140	0.69
6	γ -Chlordane	5.65	0.69	8.21	0.67	30.0	0.64	130	0.64
7	α -Chlordane	5.82	0.71	8.67	0.70	31.8	0.67	142	0.70
8	o,p' -DDE	6.84	0.84	10.3	0.84	40.5	0.86	172	0.84
9	Dieldrin	8.18	1.00	12.3	1.00	47.2	1.00	204	1.00
10	Endrin	8.94	1.09	13.6	1.09	51.6	1.09	236	1.16
11	p,p' -DDE	9.35	1.14	14.1	1.14	50.0	1.06	219	1.07
12	Perthane	11.8	1.44	17.3	1.41	62.0	1.31	278	1.36
13	o,p' -DDD	17.4	1.90	23.5	1.91	93.4	1.98	393	1.93
14	β -Endosulfan	20.0	2.70	33.2	2.69	125	2.65		
15	p,p' -DDT	26.1	3.51	43.8	3.59	138	2.94		

In order to evaluate the feasibility of these columns for the separation of basic and acidic compounds that might occur in the environment, a mixture of 2,4-dichloroaniline, 2,4-dichlorophenol and a pesticide (γ -BHC) was analysed on column 1. The pesticide and the amine gave symmetrical peaks whereas tailed peaks were obtained with the phenol. By analysing a similar mixture on column 4 at 160°, it was found that all of the compounds tested gave symmetrical peaks. On both columns plots of HETP against linear velocity were obtained by using nitrogen and hydrogen as the carrier gas; the plot for column 4 is shown in Fig. 1. By comparing the HETP values for the same compounds, it can be concluded that the use of hydrogen gives only a slight decrease in efficiency compared with the use of nitrogen but the analysis time is drastically reduced. The optimum linear gas velocity of 30 cm/sec with nitrogen becomes 80–90 cm/sec with hydrogen. A similar reduction in analysis time is observed on column 1.

By considering the capacity ratio of various compounds and by limiting the discussion to columns 1 and 4, which are characterized by a low and a high loading of stationary phase, respectively, the following conclusions can be drawn regarding the use of graphitized capillary columns. A glass capillary column with a fairly large

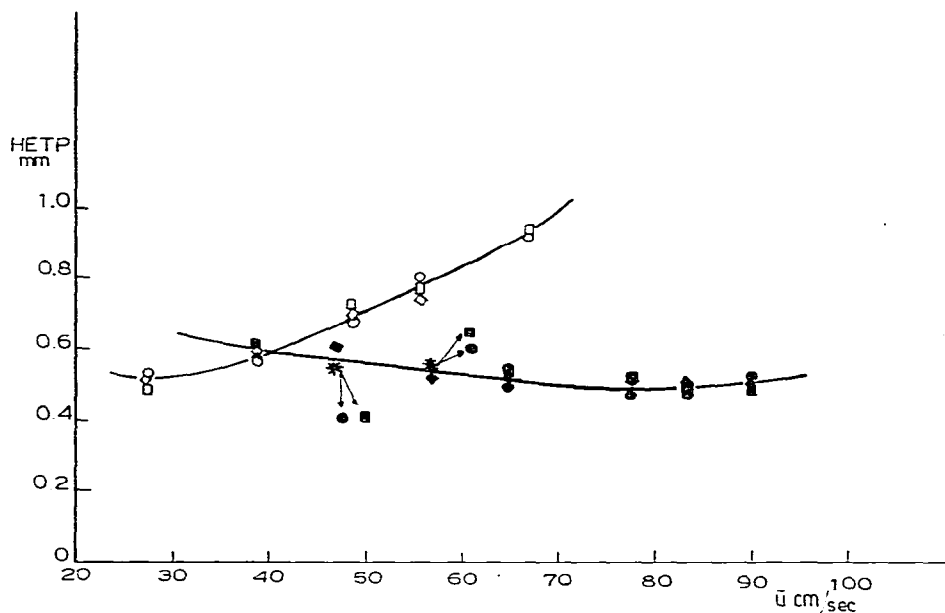


Fig. 1. HETP versus linear velocity of carrier gas at 160° in column 4. Carrier gas: open symbols, N_2 ; closed symbols, H_2 . \circ , \bullet α -BHC, $k' = 38.0$; \square , \blacksquare , 2,4-dichloroaniline, $k' = 16.6$; \diamond , \blacklozenge , 2,4-dichlorophenol, $k' = 11.2$. * represents $\blacksquare + \bullet$.

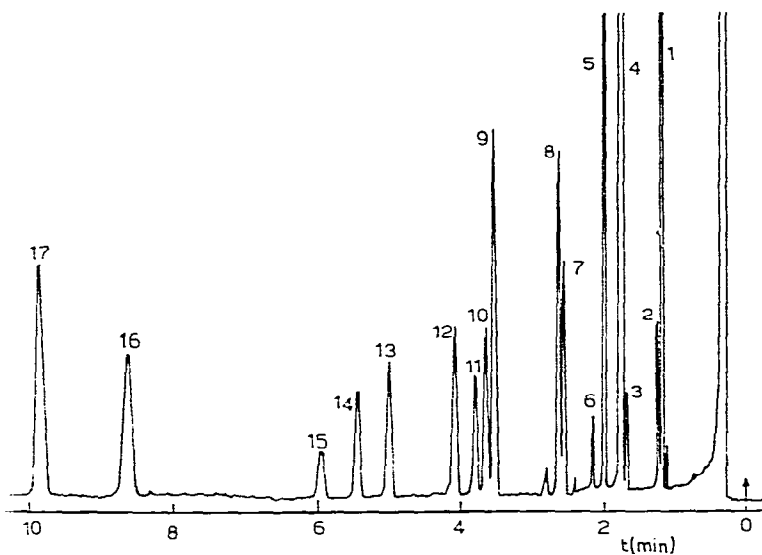


Fig. 2. Gas chromatogram of a mixture of phenols and aniline on column 4 at 160° . Carrier gas H_2 ; flame-ionization detector. Peaks: 1 = *o*-nitrophenol; 2 = *o*-chlorophenol; 3 = *o*-chloroaniline; 4 = 5-methyl-2-chloroaniline; 5 = *o*-cresol; 6 = 4-chloro-2-nitrophenol; 7 = *p*-cresol; 8 = *m*-cresol; 9 = *p*-chloroaniline + 2,4-dichlorophenol; 10 = *m*-chloroaniline; 11 = 2-methyl-3-chloroaniline; 12 = 2-methyl-4-chloroaniline; 13 = 2,4-dichloroaniline; 14 = 2,5-dichloroaniline; 15 = 2,4,6-trichlorophenol; 16 = *p*-chlorophenol; 17 = *p*-chloro-*m*-cresol.

amount of PEG 20M is particularly suitable for the analysis of volatile chlorinated compounds, phenols and amines (Fig. 2), whereas for the analysis of chlorinated compounds including the PCBs a column with a low loading of stationary phase is desirable. On the former, high-boiling compounds have very long analysis times so that their separation on such columns is not practical.

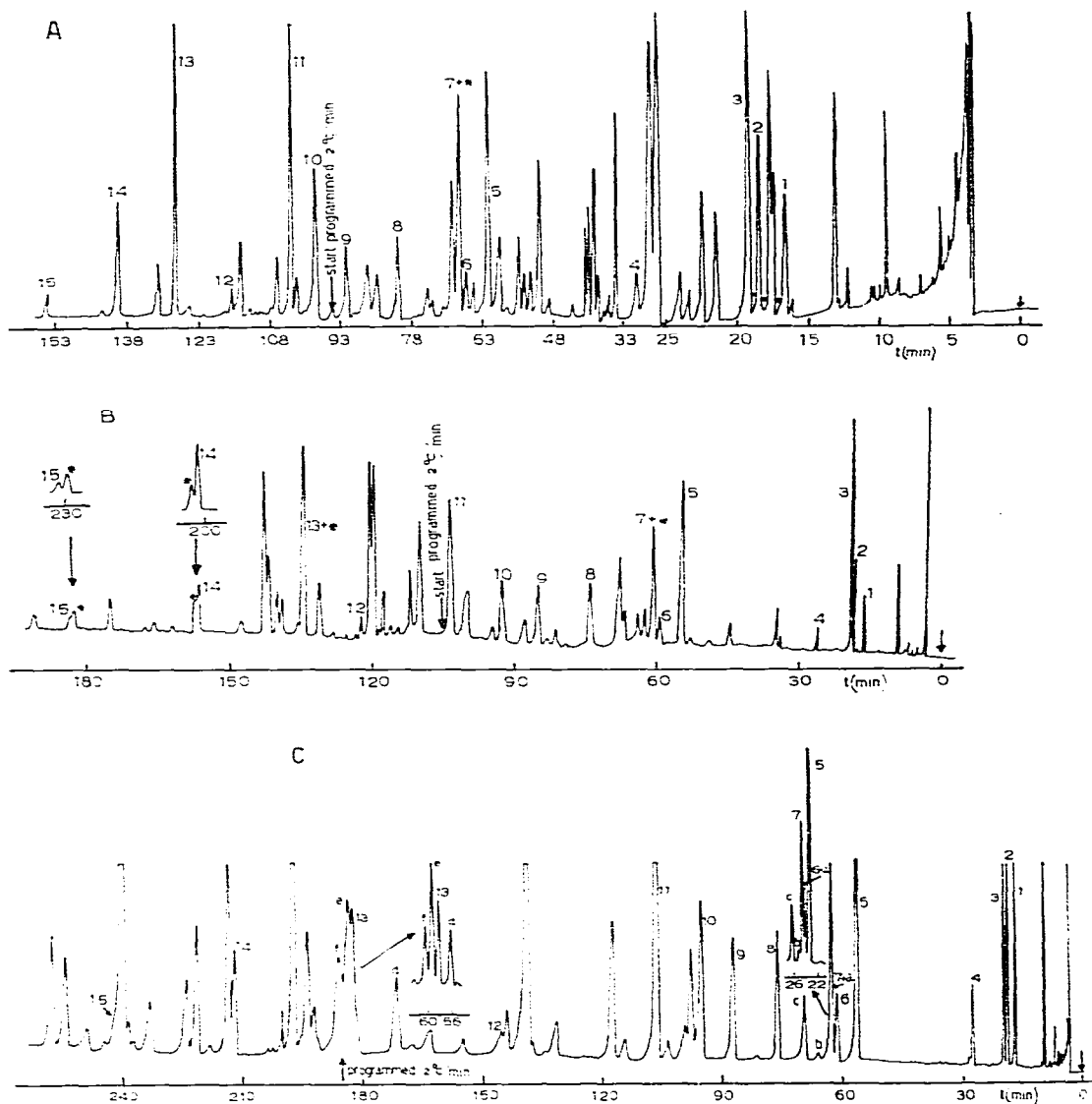


Fig. 3. Gas chromatograms of mixtures of pesticides and Aroclors on column 5. Carrier gas, H_2 ; electron-capture detector. Numbers of peaks correspond to those in Table I. (A) Aroclor 1242: temperature programme, 140° for 95 min, then increased from 140° to 160° at $2^\circ/\text{min}$. * interfering peaks. (B) Aroclor 1254: temperature programme, 140° for 105 min, then increased from 140° to 160° at $2^\circ/\text{min}$. Alternative programme: 140° for 170 min, then increased from 140° to 160° at $2^\circ/\text{min}$ (see inset peaks). * interfering peaks. (C) Aroclor 1260: temperature programme, 140° for 185 min, then increased from 140° to 160° at $2^\circ/\text{min}$. Alternative programme: isothermal at 160° (see inset peaks); a, b, c, d, e and f are peaks of Aroclor.

On the basis of these results, the separation of mixtures of chlorinated pesticides and PCB (Aroclor 1242, 1256 and 1260) was tried on column 5. This 70-m column had 210,000 theoretical plates for hexadecane at 100° (k' 2.5) and 160,000 for γ -BHC at 160° (k' 3.5). Fig. 3 shows chromatograms of complex mixtures of chlorinated organic compounds. Although the complexity of the mixture prevents the separation of all of the components, by changing the operating conditions separations of specific compounds might be achieved. As an example, the interference of some PCBs with β -endosulfan and p,p' -DDT is eliminated by varying the temperature programme (Fig. 3B). A similar situation is observed in Fig. 3C for chlordane and o,p' -DDD and is resolved by operating isothermally at 160°.

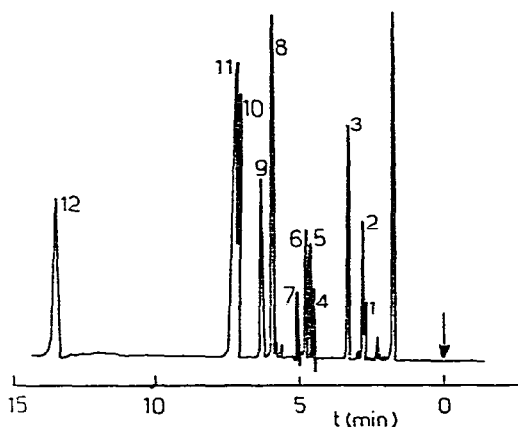


Fig. 4. Separation of halogenated anilines on column 1 at 130°. Carrier gas, N₂; electron-capture detector. Peaks: 1 = 2-chloroaniline; 2 = 2-chloro-5-methylaniline; 3 = 2-bromoaniline; 4 = 3-chloroaniline; 5 = 4-chloroaniline; 6 = 3-chloro-2-methylaniline; 7 = 4-chloro-2-methylaniline; 8 = 2,4-dichloroaniline; 9 = 2,5-dichloroaniline; 10 = 4-bromoaniline; 11 = 3-bromoaniline; 12 = 4-iodoaniline.

The results reported indicate that the thickness of the coating in graphitized capillary columns plays a predominating role. Probably columns with a low loading of stationary phase operate as gas-liquid-solid chromatographic columns and, because of the specific characteristics of graphitized carbon black, separations of chlorinated compounds of similar structure are obtained. Apparently the surface should be basic so that amines yield symmetrical peaks (Fig. 4). The behaviour of capillary columns with a high loading of stationary phase should be considered typical of gas-liquid chromatography.

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