

GAS-LIQUID CHROMATOGRAPHY OF SOME CONDENSED-RING AROMATIC HYDROCARBONS ON LIGHTLY-LOADED COLUMNS

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INTRODUCTION

We wished to chromatogram some condensed-ring aromatic hydrocarbons, with boiling points up to 450° , on a conventional commercial apparatus (a Pye Argon Chromatograph) with a maximum column temperature of 225° . It has already been shown¹⁻⁴ that by the use of very sensitive detectors and by reduction of the percentage of stationary phase on the inert support, retention times of high boiling materials may be reduced to workable values. SWEETING AND WILSHIRE³, for instance, successfully chromatographed compounds up to 1,6-diphenylhexane, b.p. 348° , on a 4 ft. column of 5 % apiezon L at 180° . Accordingly we have studied the chromatography of these condensed-ring hydrocarbons on lightly-loaded columns at temperature from 175° to 225° , with both glass beads and Celite 545 as inert supports, on three stationary phases.

EXPERIMENTAL

The apparatus used was a Pye Argon chromatograph. Columns of glass, were all $120\text{ cm} \times 5\text{ mm}$ (I.D.), packed by tamping on a stone floor. Stationary phases were applied in the usual way; when preparing stationary phases on glass beads, the phase was dissolved in a suitable solvent and then mixed with, and stripped from, the glass beads in as small a vessel as possible, thus minimising the amount of phase lost to the glass vessel. All percentages of stationary phase to inert support are calculated on a w/w basis.

Solutes were applied as $0.1\ \mu\text{l}$ of approx. 10 % solutions in 1-methylnaphthalene; for the higher molecular weight hydrocarbons it was necessary to dissolve them in hot 1-methylnaphthalene.

Retention times are expressed relative to pyrene (100), and retention times relative to pyrene will be denoted by τ . Column efficiencies were measured in terms of theoretical plates⁵ and expressed as HETP.

Solutes were reagent chemicals. Stationary phases were as follows: Apiezon L (Edwards High Vac. Ltd.), Silicone oil (May and Baker "Embaphase") and Polystyrene (kindly provided by Mr. M. S. ALGER, and having $\bar{M}_v = 6 \cdot 10^4$, and $[\eta] = 0.312$ in toluene at 25°).

RESULTS AND DISCUSSION

(a) Glass bead supports

A careful study by LITTLEWOOD⁶ has shown that HETP values down to 0.9 mm can be obtained with glass beads as the solid support. LITTLEWOOD found that for a column of 1% tricresyl phosphate on 150–200 mesh glass beads at temperatures about 80°, the minimum value of HETP, $(HETP)_{min}$, occurred at gas flow rates as low as 10–15 ml/min. Somewhat different results were obtained by FREDERICK, MIRANDA AND COOKE⁷ who found that for 0.16% silicone on glass beads at 74°, $(HETP)_{min}$ occurred at much higher flow rates: 70 ml/min for 70–80 mesh beads, and 69 ml/min for 140–230 mesh beads. Other workers have also used quite high flow rates for analyses on 0.1% dinonyl phthalate or 0.1% silicone grease on glass beads (55–90 ml/min)⁸ or on 0.125% apiezon L on glass beads (42–52 ml/min)².

We have found that columns of 0.1 to 0.2% silicone oil or polyethylene glycol adipate on glass beads give very poor chromatograms, but that satisfactory separations could be achieved on columns of 0.1 to 0.2% apiezon L or polystyrene on 48–66 mesh glass beads. Like LITTLEWOOD, we found that $(HETP)_{min}$ for these columns occurs at very low flow rates (Fig. 1) and this considerably reduces the usefulness of these columns, especially as the HETP increases substantially with increase in flow rate.

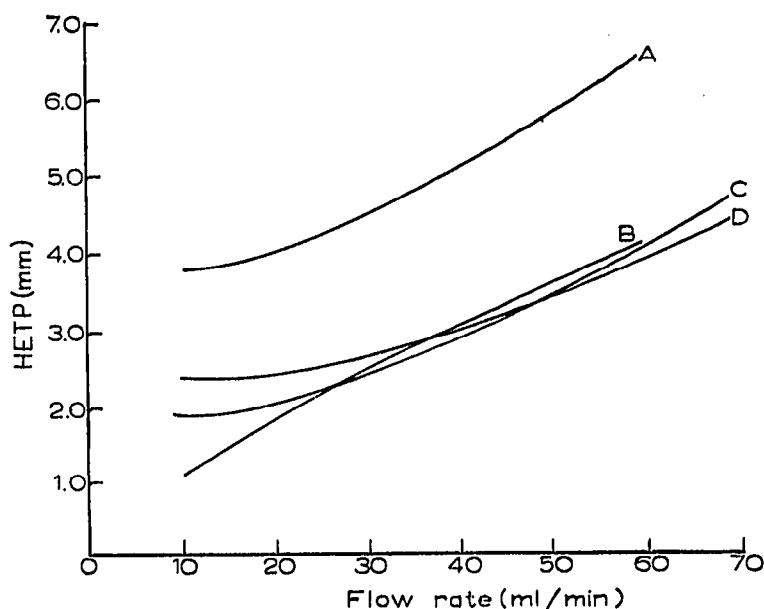


Fig. 1. (A) 0.2% apiezon L; 225°; pyrene (R_t at 30 ml/min = 2.5 min). (B) 0.2% polystyrene; 225°; 2:3-benzofluorene (R_t at 30 ml/min = 5.6 min). (C) 0.27% apiezon L; 175°; anthracene (R_t at 30 ml/min = 11 min). (D) 0.2% apiezon L; 225°; anthracene (R_t at 30 ml/min = 8 min).

Furthermore, as the packing density of 48–66 mesh glass beads is about six times that of 48–66 mesh celite 545, a given percentage of stationary phase on the glass beads will give retention times equivalent to those obtained with a six times as great a percentage stationary phase on celite. For instance, at 175° with a flow rate of 40 ml/min and on columns of identical lengths and diameters, anthracene is eluted after 13.4 min on 2.0% apiezon L on celite 545 (48–66 mesh) and after 8.4 min on 0.27% apiezon L on glass beads (48–66 mesh).

We concluded that for condensed-ring aromatic hydrocarbons, better separations

and more useful analyses could be obtained by the use of lightly-loaded columns with celite 545 as the solid support.

(b) *Celite supports*

Plots of HETP vs. flow rate are shown in Fig. 2 for columns of 2% apiezon L, 2% silicone oil and 4% polystyrene on celite. Solutes were chosen for these determinations so that as far as possible their retention times (at a standard flow rate of 30 ml/min) were the same. Both apiezon L and polystyrene were very satisfactory: not only does $(\text{HETP})_{\text{min}}$ occur at a higher flow rate than for the glass bead columns, but also only little loss in efficiency takes place on increasing the flow rate to 50 or 60 ml/min.

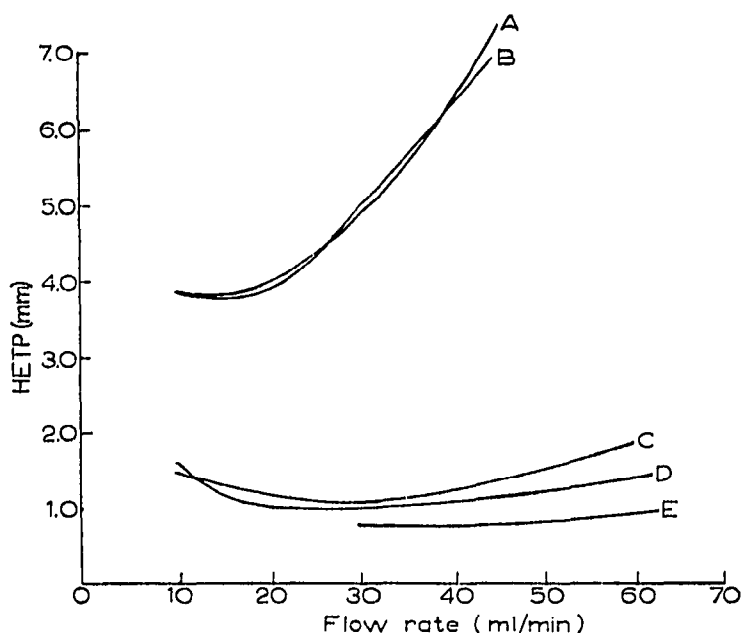


Fig. 2. (A) 2% silicone oil; 200°; 2:3-benzofluorene (R_t at 30 ml/min = 8.2 min). (B) 2% silicone oil; 175°; fluoranthene (R_t at 30 ml/min = 8.2 min). (C) 2% apiezon L; 175°; fluorene (R_t at 30 ml/min = 6.9 min). (D) 4% polystyrene; 200°; anthracene (R_t at 30 ml/min = 14 min). (E) 2% apiezon L; 225°; 2:3-benzofluorene (R_t at 30 ml/min = 17.7 min).

Tailing on these two columns was not marked. Columns of 2% silicone oil on celite were much less satisfactory; however, as the retention times of the condensed-ring aromatics were much lower on silicone oil than on apiezon L or polystyrene, we were able to use higher percentages of stationary phase in the case of silicone oil.

(c) *Relative retention times*

Table I gives retention times relative to pyrene (100) on columns of 2% apiezon L, 4% polystyrene and 2–10% silicone oil. We observed no change in relative retention times on silicone oil columns with different percentages of stationary phase, and the retention times quoted for silicone oil are the combined averages of results from a 2% and a 10% column.

(i) *On apiezon L.* A plot of $\log \tau$ vs. carbon number for compounds 1 to 13 is linear with some degree of scatter, no doubt because these compounds do not form a homologous series. Both retene and 2-phenylnaphthalene lie well off the best straight line

TABLE I

RETENTION TIMES OF CONDENSED-RING AROMATIC HYDROCARBONS RELATIVE TO PYRENE

No.	Hydrocarbon	B.p. °C	Polystyrene		Apiezon L		Silicone oil	
			200 ^a	225 ^b	175 ^c	225 ^d	175 ^e	200 ^f
1	Naphthalene	218	1.5	—	0.9	—	2.9	4.4
2	1-Methylnaphthalene	245	2.6	3.6	2.1	3.4	4.7	6.3
3	Acenaphthylene	277	5.8	8.0	4.3	6.6	8.6	12.3
4	Fluorene	298	9.5	11.9	8.2	11.2	14.1	18.0
5	Phenanthrene	336	24.6	27.6	23.2	27.0	31.7	36.7
6	Anthracene	340	25.8	28.6	23.4	28.2	31.7	36.7
7	Fluoranthene	383	79.3	79.3	78.8	79.3	84.9	86.2
8	Pyrene	393	100	100	100	100	100	100
9	2:3-Benzofluorene	407	150	139	155	138	153	147
10	Chrysene	440	—	338	—	317	332	294
11	Triphenylene	438	—	344	—	320	—	291
12	1:2-Benzanthracene	437	—	332	—	308	—	307
13	Naphthacene	ca. 450	—	377	—	363	—	324
14	Retene	390	94.5	90.4	133	114	154	147
15	2-Phenylnaphthalene	360	45.9	50.7	47.5	49.4	62.0	65.5
16	Hexadecane	287	2.1	2.5	6.0	7.9	16.5	17.8
17	Octadecane	317	4.4	4.5	16.2	15.8	38.5	39.0

Retention time for pyrene at 45 ml/min:

- ^a 4.5 % polystyrene; 34.8 min
^b 4.5 % polystyrene; 13.6 min
^c 2.0 % apiezon L; 50.6 min
^d 2.0 % apiezon L; 8.7 min
^e 2.0 % silicone oil; 9.0 min
 10.0 % silicone oil; 68.3 min
^f 2.0 % silicone oil; 3.6 min
 10.0 % silicone oil; 26.0 min.

on the side of the hexadecane–octadecane line. However, a plot of $\log \tau$ vs. b.p. gives a straight line for compounds 1 to 17 on which only retene does not lie. Anthracene and phenanthrene are not resolved, and of the C₁₈ fused ring aromatics (10–13) only the pair 1:2-benzanthracene/naphthacene are completely resolved at 225°. At a flow rate of 60 ml/min at 225° naphthacene (b.p. ca. 450°) has a retention time of only 23 min on 2 % apiezon L.

Relative retention times have previously been quoted for compounds³ 1 to 5 on apiezon L at 180° and for compounds⁹ 4, 5, 6 and 10 at 235°; these results agree quite well with ours. CARUGNO AND GIOVANNOZZI-SERMANNI¹⁰ have recorded retention data on apiezon L for compounds 1 to 8 at 230° and compounds 8, 10 and 12 at 260°, as well as retention data for several higher condensed ring systems at 260°. Where comparisons can be made, however, these results do not agree very well with either our results or those found previously.

(ii) *On silicone oil.* Plots of $\log \tau$ vs. b.p. or carbon number for compounds 1 to 13 again produce a straight line with some scatter. Retention times on silicone oil are much smaller than on apiezon L; at 175° fluoranthene is eluted on 2 % apiezon L after 45 min, and on 2 % silicone oil after only 6.8 min, the flow rate being 40 ml/min in each case.

DUPIRE AND BOTQUIN¹¹ have recorded retention times for compounds 1 to 8 and compound 10 on silicone at 235° and 295°, and SOLO AND PELLETIER⁹ have chromato-

graphed compounds 4, 5, 6, 10 and 12 at the same temperatures. With the exception of DUPIRE AND BOTQUIN's result for chrysene at 295°, these results agree with each other and with the retention times that we have obtained.

(iii) *On polystyrene.* Compounds 1 to 13 show much scatter when plotted as $\log \tau$ vs. carbon number. However, a plot of $\log \tau$ vs. b.p. gives a much better line on which compounds 1 to 15 all lie. As with apiezon L, only the compounds 1: 2-benzanthracene and naphthacene are completely resolved at 225°. Polystyrene shows appreciably more selectivity towards aromatics over aliphatics than does apiezon L and we feel that it should make a useful addition to the comparatively small number of high temperature stationary phases that are available. The efficiency of the polystyrene columns, though, dropped drastically below about 190°; possibly this is due to a viscosity effect.

(iv) *Identification plots.* A plot of $\log \tau$ (polystyrene) vs. $\log \tau$ (apiezon L) or a plot of $\log \tau$ (apiezon L) vs. $\log \tau$ (silicone oil) give straight line plots on which compounds 1-13 all lie. The non-condensed aromatic, 2-phenylnaphthalene also lies on both of these straight lines, but the side chain compound, retene (8-methyl-2-isopropylphenanthrene) falls just off the straight line. For identification of the condensed-ring aromatic hydrocarbons, a much better method is to plot $\log \tau$ (polystyrene) vs. $\log \tau$ (silicone oil). As can be seen from Fig. 3, all the hydrocarbons 2-13 lie on the straight

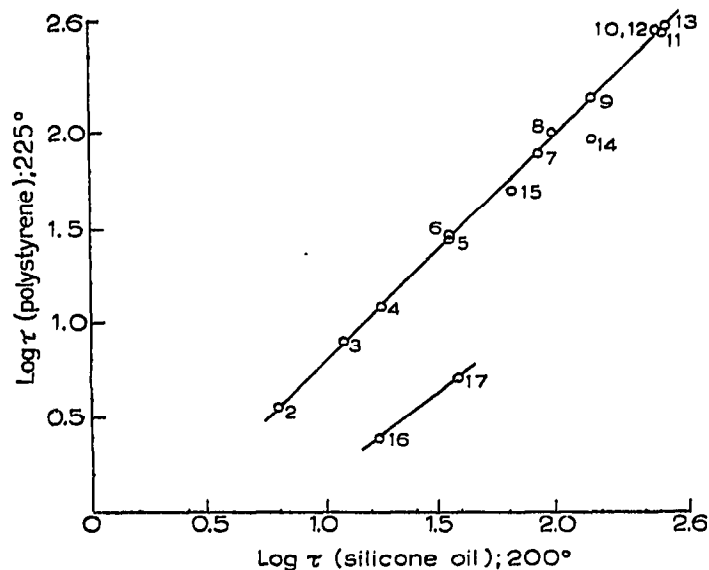


Fig. 3. Retention data taken from Table I.

line, retene is well displaced from the line and 2-phenylnaphthalene also lies just off the straight line.

ACKNOWLEDGEMENT

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SUMMARY

Gas-liquid chromatography on lightly-loaded columns with Celite 545 as the support provides a rapid and satisfactory method of identification of condensed ring aromatic hydrocarbons up to and including naphthacene, at elution temperatures of 175° to 225°. No special equipment is required for these analyses.

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