

## GAS-CHROMATOGRAPHIC ANALYSIS OF POLYNUCLEAR ARENES

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## INTRODUCTION

The analysis of polynuclear arenes is difficult because it usually involves the separation of the arenes from adventitious matter followed by partial or complete (liquid phase) chromatographic resolution into the individual compounds<sup>1-11</sup>. The identity of the "isolated" compound has invariably been deduced from spectroscopic data, usually from the ultra-violet absorption spectrum. This sequence is extremely time-consuming and requires very careful work. Moreover, the quantitative nature of the analysis is suspect since an isotope experiment has shown that losses can be as high as 50 %<sup>8</sup>.

The methods referred to above were developed for analysing mixtures which contain predominantly the unsubstituted polynuclear arenes; they are not appropriate to systematic investigation of the alkyl derivatives which are of interest in the study of carcinogenesis<sup>12-14</sup> and of low-temperature pyrolysis.

The gas-chromatographic analysis of polynuclear arenes has been described by a number of workers, including DUPIRE<sup>15-18</sup>, who chromatographed certain of the polynuclear hydrocarbons during work on the constitution of coal tar. He used a thermal-conductivity detector and worked at temperatures which cause substrate bleeding (ionization detector). CARUGNO AND GIOVANNOZZI-SERMANNI<sup>19</sup> analysed some of the polynuclear arenes with a low-resolution system having a detector of limited sensitivity (copper oxide combustion-thermal conductivity). GUDZINOWICZ AND SMITH<sup>20</sup> chromatographed triphenylene, picene and coronene. Sensitivity and resolution were low. FERRERO<sup>21, 22</sup> analysed polynuclear arenes in coal tar. He used a thermal-conductivity detector and collected fractions for subsequent study. WOOD<sup>23</sup> also has analysed a coal tar-polynuclear arenes mixture using an emissivity detector. SAUERLAND<sup>24, 25</sup> employed programmed-temperature chromatography in a study of the polynuclear arenes from coal tar fractions, using a thermal-conductivity detector and columns of low efficiency. FARRAND<sup>26</sup> attempted to analyse a coal tar polynuclear arene fraction using columns of low efficiency and a thermal-conductivity detector. LIJINSKY *et al.*<sup>27</sup> and LIJINSKY AND MASON<sup>28</sup> chromatographed polynuclear arenes on a glass-bead column using an ionization (argon?) detector. The column efficiency was low.

These methods are not suited to the *low-level analysis* of the complex mixtures of polynuclear arenes generally encountered in pollution studies and in other cases where the sample is limited in size.

During the analysis of a low-temperature pyrolysate<sup>29</sup> (from cholesterol) the

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present author found it necessary to determine methylchrysenes and alkylphenanthrenes in the presence of the parent compounds. Gas chromatography proved to be the most satisfactory of the methods tried; the technique has now been in use for some three years and has been extended to the analysis of higher systems.

## EXPERIMENTAL

A laboratory-built instrument (with flame ionization detector and column outlet splitter) was used for the packed-column study, and a Perkin-Elmer model 154 chromatograph for the capillary column analyses. The injection block heater of the latter was disconnected (since it operated at pyrolytic temperatures) and replaced by an independently controlled heater.

The packed columns were of stainless steel, type 304, non-passivated, 4 mm and 2 mm I.D. The columns were helical, of 8 cm diameter.

The stationary phases were SE-30 and SE-52 (10 % by weight on the support) and Q-F1 (2.5 % by weight on the support). The support was of Chromosorb W, acid-washed, 60-80 mesh.

The fraction collectors were Pyrex tubes (10 cm  $\times$  2 mm, and 10 cm  $\times$  1 mm).

The capillary columns were of stainless steel, type 347, 0.5 mm and 1.0 mm I.D., coated with SE-30 from 5 % solution in chloroform.

For sample introduction a toluene solution (0.1-2.0 %) was used, injected with a micro-syringe.

## RESULTS

### *Packed columns*

Monel tubing was found to exhibit catalytic effects toward a number of hydroaromatic compounds, and copper was adsorptive for the polynuclear arenes. Stainless steel did not show these effects.

The tetracyclic and higher polynuclear arenes were adsorbed, to a slight degree, by the support; this did not produce tailing at the  $10^{-6}$  g level. However, chrysene and benz(a)anthracene, while giving acceptably symmetrical peaks, were detectable (in the ultra-violet spectrum of a collected fraction) subsequent to the peak. The penta- and hexa-cyclic compounds, also, gave good peaks; the adsorbed material was, however, eluted only by displacement (by a similar or more highly condensed compound). The eluted compound was then seen in the ultra-violet spectrum of the displacing compound. The indicated adsorption level was  $10^{-9}$  g/g support, which is of little significance in the analysis of samples of the order of  $10^{-6}$  g.

Glass-bead packings proved too inefficient (HETP  $\sim$  4 mm) for the analysis, although adding finely divided kieselguhr<sup>30</sup> to the packing resulted in an increase in the column efficiency (to an HETP of 1.4 mm). The necessarily high inlet pressures limited the length, and hence the efficiency, of the column; the maximum practical efficiency was some four times less than that of the Chromosorb-packed column. Adsorption (see above) was not detectable in an SE-30 glass-bead-in-stainless-steel column.

A loss of efficiency occurred when a newly conditioned (helical) column was allowed to cool (from an HETP of 0.8 to 1.2-1.4 mm for a 10 m SE-30 column cooling

TABLE I  
RETENTION DATA<sup>a</sup> OF ARENES ON SE-30

| Compound <sup>b</sup>                                 | Column temperature (°C) |                  |
|---|-------------------------|------------------|
|   | 260                     | 300              |
| Fluorene  | 28                      | 32.6             |
| 2-Methylfluorene                                      | 36.6                    | 40.7             |
| Anthracene  | 45.7                    | 50               |
| Phenanthrene  | 45.3                    | 50               |
| 3-Methylphenanthrene                                  | 56                      | 61.4             |
| 1-Methylphenanthrene                                  | 62.5                    | 66.3             |
| 4,5-Methylenephenanthrene                             | —                       | 67.1             |
| 9-Methylanthracene                                    | 68.1                    | 70.9             |
| 1-Ethylphenanthrene                                   | 75.1                    | 76.4             |
| Fluoranthrene   | 87.4                    | 88.3             |
| Pyrene  | 100 <sup>c</sup>        | 100              |
| 2-Methylpyrene  | 129                     | 122              |
| 4-Methylpyrene  | 138                     | 131              |
| 1-Methylpyrene  | 140                     | 133              |
| Benzo(a)fluorene                                      | 121                     | 116              |
| Benzo(b)fluorene                                      | 125                     | 119              |
| Benzo(c)fluorene                                      | 126                     | 119              |
| 16,17-Dihydro-15H-cyclopenta(a)phenanthrene           | 134                     | 127              |
| 17-Methyl-16,17-dihydro-15H-cyclopenta(a)phenanthrene | 146                     | 135              |
| 17-Methyl-15H-cyclopenta(a)phenanthrene               | 176                     | 161              |
| Benzo(g,h,i)fluoranthene                              | 184                     | 168              |
| Triphenylene  | 207                     | 182              |
| Chrysene  | 208                     | 183              |
| Benz(a)anthracene                                     | 207                     | 183              |
| Naphthacene   | 221                     | 195              |
| 2-Methylchrysene                                      | 272                     | 233              |
| 3-Methylchrysene                                      | 268                     | 231              |
| 4-Methylchrysene                                      | 279                     | 236              |
| 6-Methylchrysene                                      | 283                     | —                |
| 1-Methylchrysene                                      | 289                     | 243              |
| 1-Methylbenz(a)anthracene                             | —                       | 264 <sup>d</sup> |
| 9-Methylbenz(a)anthracene                             | —                       | 272 <sup>d</sup> |
| 10-Methylbenz(a)anthracene                            | —                       | 247 <sup>d</sup> |
| 3-Methylbenz(a)anthracene                             | —                       | 272 <sup>d</sup> |
| 4-Methylbenz(a)anthracene                             | —                       | 278 <sup>d</sup> |
| 7-Methylbenz(a)anthracene                             | 302                     | 302 <sup>d</sup> |
| Benzo(b)fluoranthene                                  | 401                     | —                |
| Benzo(h)fluoranthene                                  | 404                     | —                |
| Benzo(e)pyrene  | 458                     | 364              |
| Benzo(a)pyrene  | 472                     | 374              |
| Perylene  | 492                     | 385              |
| 3-Methylcholanthrene                                  | 585                     | 439              |
| Indeno(1,2,3-c,d)fluoranthene <sup>e</sup>            | 766                     | —                |
| Indeno(1,2,3-c,d)pyrene <sup>e</sup>                  | 875                     | —                |
| Dibenz(a,h)anthracene                                 | 896                     | 632              |
| Benzo(c)tetraphene                                    | 927                     | 654              |
| Picene  | 931                     | 663              |
| Benzo(g,h,i)perylene                                  | 988                     | 711              |
| Anthanthrene  | 1050                    | 753              |
| Coronene  | —                       | 1350             |

<sup>a</sup> Relative to pyrene = 100; 10 m and 2 m columns.

<sup>b</sup> The nomenclature adopted for this paper is that recommended by I.U.P.A.C. (1957).

<sup>c</sup> Approximately 20 min.

<sup>d</sup> Extrapolated values.

<sup>e</sup> Identity based on ultraviolet spectrum of relevant fraction.

from 300° to ambient temperature). This effect, which was not cumulative, was not observed during subsequent heating cycles, and in straight or U-form columns was not significant. (It is considered that this loss of efficiency is due to mechanical stress applied to the packing during the coiling process.)

The stationary phases SE-30 and SE-52 were used up to 300°, which was found to be the upper limit for high-sensitivity analysis with the flame-ionization detector. The stationary phase Q-FI was used up to 225°.

Retention data for the packed columns are given in Tables I-IV.

TABLE II  
RETENTION DATA\* OF ARENES ON SE-52

| Compound   | Column temperature (°C) |     |
|--|-------------------------|-----|
|  | 260                     | 300 |
| Fluorene   | 25                      | 30  |
| 2-Methylfluorene   | 33                      | 38  |
| Phenanthrene   | 43                      | 48  |
| 3-Methylphenanthrene   | 56                      | 59  |
| 1-Ethylphenanthrene  | 73                      | 74  |
| Fluoranthene   | 87                      | 87  |
| Pyrene   | 100                     | 100 |
| 1-Methylpyrene   | 135                     | 131 |
| Benzo( <i>b</i> )fluorene                                      | 125                     | —   |
| Benzo( <i>c</i> )fluorene                                      | 125                     | —   |
| 17-Methyl-16,17-dihydro-15H-cyclopenta( <i>a</i> )phenanthrene | 146                     | 134 |
| Triphenylene   | —                       | 189 |
| Chrysene   | 216                     | 190 |
| Benz( <i>a</i> )anthracene                                     | 209                     | 186 |
| Naphthacene  | 230                     | 203 |
| 2-Methylchrysene   | 276                     | 240 |
| 3-Methylchrysene   | 276                     | 240 |
| 4-Methylchrysene   | 292                     | 245 |
| 6-Methylchrysene   | 290                     | —   |
| 1-Methylchrysene   | 300                     | 252 |
| 7-Methylbenz( <i>a</i> )anthracene                             | 315                     | 262 |
| Benzo( <i>e</i> )pyrene  | 494                     | —   |
| Benzo( <i>a</i> )pyrene  | 512                     | —   |
| Perylene   | 538                     | —   |

\* Relative to pyrene = 100.

#### Capillary columns

The minimum tube diameter of 0.5 mm was dictated by the high viscosity of solutions (chloroform) of the phase SE-30.

The tetra- and penta-cyclic arenes were adsorbed (tailing) to a significant degree but this effect decreased when the film thickness was increased (by coating from a 5% instead of a 1% solution). As a result, the resolving power of the column for *n*-alkanes was decreased (from 1.0 to 0.78, HETP of 1.2 mm and 2.2 mm) whilst that for the arenes was increased (from 0.50 to 0.70 relative to the above figures).

Optimum resolution was attained for samples (on column) of  $2 \cdot 10^{-7}$  to  $10^{-6}$  g.

The columns have been used for prolonged periods (more than 3 months) at 260° without loss of efficiency.

The retention data for the capillary column are given in Table V.

TABLE III

RETENTION DATA\* OF ARENES ON Q-FI\*\*

| Compound  | Column temperature (°C) |      |
|---|-------------------------|------|
|   | 200                     | 220  |
| Fluorene  | 16                      | —    |
| 2-Methylfluorene                                      | 22                      | —    |
| Anthracene  | 35                      | —    |
| Phenanthrene  | 34                      | —    |
| 3-Methylphenanthrene                                  | 48                      | —    |
| 4,5-Methylenephenanthrene                             | 48                      | —    |
| 2-Methylanthracene                                    | 50                      | —    |
| 9-Methylanthracene                                    | 54                      | —    |
| 1-Ethylphenanthrene                                   | 60                      | —    |
| Fluoranthene  | 87                      | 88   |
| Pyrene  | 100                     | 100  |
| 4-Methylpyrene  | 143                     | —    |
| 1-Methylpyrene  | 148                     | —    |
| 3-Methylpyrene  | 151                     | —    |
| Benzo(a)fluorene                                      | 115                     | 122  |
| Benzo(b)fluorene                                      | 123                     | —    |
| Benzo(c)fluorene                                      | 126                     | —    |
| 16,17-Dihydro-15H-cyclopenta(a)phenanthrene           | 121                     | —    |
| 17-Methyl-16,17-dihydro-15H-cyclopenta(a)phenanthrene | 133                     | —    |
| 17-Methyl-15H-cyclopenta(a)phenanthrene               | 187                     | —    |
| Triphenylene  | 264                     | —    |
| Chrysene  | 263                     | 245  |
| Benz(a)anthracene                                     | 262                     | —    |
| Naphthacene   | 284                     | 267  |
| 2-Methylchrysene                                      | 376                     | —    |
| 3-Methylchrysene                                      | 374                     | —    |
| 4-Methylchrysene                                      | 348                     | 318  |
| 6-Methylchrysene                                      | 384                     | —    |
| 1-Methylchrysene                                      | 390                     | 356  |
| 7-Methylbenz(a)anthracene                             | 409                     | 372  |
| Benzo(e)pyrene  | —                       | 668  |
| Benzo(a)pyrene  | —                       | 729  |
| Perylene  | —                       | 751  |
| Benzo(c)tetraphene                                    | —                       | 1600 |
| Picene  | —                       | 1610 |
| Benzo(g,h,i)perylene                                  | —                       | 1760 |
| Anthanthrene  | —                       | 1910 |

\* Relative to pyrene = 100.

\*\* 2.5%, 10 m and 2 m column.

1.0 mm capillary columns gave an HETP of 10 mm for chrysene at 200° with a sample load of  $10^{-5}$  g. An outlet splitter was used, and fractions were collected for spectrophotometry.

#### Fraction collection

Fractions were collected in air-cooled glass tubes, the smaller of which (1 mm I.D.) were used for immediate melting-point determinations.

The collection efficiency was about 70% for phenanthrene and the higher arenes at the  $10^{-6}$  to  $2 \cdot 10^{-5}$  g level but decreased to 50–60% at  $10^{-4}$  g because of fog formation. The recovery of the larger samples was improved (to 85–95%) by electrostatic

TABLE IV

RELATIVE RETENTION TIMES OF ARENES ON SE-30 ON GLASS BEADS AT 200°

| Compound          | Column        |      |      |
|-------------------|---------------|------|------|
|                   | (a)           | (b)  | (c)  |
| Pyrene            | 1.00 (12 min) | 1.00 | 1.00 |
| Triphenylene      | 2.78          | 2.75 | 2.78 |
| Benz(a)anthracene | 2.77          | 3.25 | 2.77 |
| Chrysene          | 2.81          | 3.5  | 2.81 |

(a) 2 m, 4 mm I.D., s/s (type 304) or 1 m, 3 mm I.D., Pyrex; 0.25% SE-30 on glass beads, 80-100 mesh.

(b) LIJINSKY *et al.*<sup>27</sup>, 2.44 m (copper?); 0.25% SE-30 on glass beads.

(c) 2 m, 4 mm I.D., s/s (type 304), 10% SE-30 on Chromosorb W, acid washed, 80-100 mesh.

TABLE V

RELATIVE RETENTION TIMES OF ARENES ON CAPILLARY COLUMNS

| Compound                  | Column temperature (°C) |      |      |      |
|---------------------------|-------------------------|------|------|------|
|                           | 260                     |      | 235  |      |
|                           | (a)                     | (b)  | (c)  | (d)  |
| Fluorene                  | *                       |      | 0.24 |      |
| 2-Methylfluorene          | *                       |      | 0.32 |      |
| Phenanthrene              | 0.44                    | 0.45 | 0.42 |      |
| Anthracene                |                         |      | 0.42 |      |
| 3-Methylphenanthrene      | 0.56                    | 0.56 | 0.55 |      |
| 4,5-Methylenephenanthrene |                         |      | 0.60 |      |
| 9-Methylanthracene        |                         |      | 0.67 |      |
| Fluoranthene              | 0.87                    | 0.87 | 0.87 |      |
| Pyrene                    | 1.00**                  | 1.00 | 1.00 | 1.00 |
| 4-Methylpyrene            | 1.38                    | 1.38 | 1.43 |      |
| 1-Methylpyrene            |                         |      | 1.46 |      |
| 2-Methylpyrene            |                         |      | 1.34 |      |
| Benzo(a)fluorene          | 1.22                    | 1.21 |      |      |
| Triphenylene              |                         |      | 2.25 | 2.25 |
| Chrysene                  | 2.08                    | 2.08 | 2.27 | 2.28 |
| Benz(a)anthracene         |                         |      | 2.24 | 2.24 |
| 4-Methylchrysene          | 2.80                    | 2.79 | 3.13 | 3.15 |
| Benzo(e)pyrene            | 4.60                    | 4.58 | 5.43 | 5.45 |
| Benzo(a)pyrene            | 4.72                    | 4.72 |      |      |

(a) and (c) 60 m, 0.5 mm I.D., s/s (type 347), SE-30 (*n*,  $5 \cdot 10^4$ , *n*-tetracosane; *n*,  $2 \cdot 10^4$ , chrysene); (b) and (d) standard SE-30 analytical column.

\* Retention times not accurately reproducible.

\*\* 5 minutes.

precipitation, by scrubbing the gas by passing it through glass helices which were wet with ethanol at  $-20^\circ$ , or by passing the gas through coarse (30 mesh) Celite.

Ultra-violet spectra have been determined as a routine procedure on injected samples of  $2 \cdot 10^{-6}$  g for all the unsubstituted arenes of Table I from phenanthrene to coronene.

*Detector response*

The relative (flame ionization) detector response for the polynuclear arenes of Table I was found to vary by some  $\pm 5\%$  depending on the sample size and the history of the column. In no case did it differ from unity by more than 10%.

## DISCUSSION

Evidently many of the polynuclear arenes can be resolved by gas chromatography under conditions attainable in a well-regulated chromatograph which is fitted with a sensitive (ionization) detector. The technique can be applied to samples of  $10^{-6}$  g and less, a sensitivity which compares favourably with that of the liquid chromatographic methods.

For some purposes gas-chromatographic separation *alone* is adequate<sup>31</sup>, but if (as is often the case) it is necessary, the concentrations of the unresolved components can be found either from the ultra-violet spectrum of the gas-chromatographic fraction (in a favourable case, such as that of the chrysene-benz(*a*)anthracene mixture) or by subsequent resolution (see below) of the fraction and determination of the ultra-violet spectra.

The following analytical scheme has proved satisfactory:

(1) Chromatography on alumina or silica gel, which serves to concentrate the polynuclear arenes.

(2) High-resolution gas chromatography on the phase SE-30, with the collection of fractions for ultra-violet spectrophotometry.

(3) (If necessary) chromatography on acetylated paper or acetylated cellulose of those fractions which are shown to be mixtures, and subsequent determination of the ultra-violet spectra of the resolved components.

This scheme has the advantage that the precision chromatography on the difficultly reproducible materials alumina, silica gel, and acetylated cellulose is replaced by high-efficiency gas chromatography, the reproducibility of which is good. Those compounds which are not resolved on SE-30 are readily separated on acetylated cellulose or acetylated paper (Table VI).

In qualitative analysis it is useful to know the relation between log (relative retention time) and carbon number (Fig. 1). It is apparent, however, that an alkyl carbon does not produce as great a log (retention time) increment as does a ring carbon. The retention values for the more highly alkylated arenes cannot therefore be derived from the data of Fig. 1.

The method outlined has given good quantitative results using the flame-ionization detector. Preliminary work has shown that the argon detector also is capable of giving an acceptable degree of precision. A disparity in detector response similar to that which LIJINSKY AND MASON<sup>28</sup> reported for the compounds pyrene and dibenz(*a,h*)anthracene (response values of about 1 and 0.01 respectively) has not been observed in this work with either the flame-ionization detector or the argon detector.

The retention values for the arenes have been found to be reproducible on three chromatographs provided that all are operated at the same temperature and not merely at the same *indicated* temperature. The effect of a difference in column temperature can, however, be minimized by the use of a retention reference compound with a retention volume close to that of the compound being studied.

TABLE VI

COMPARISON OF  $R_F$  VALUES OF ARENES ON ACETYLATED PAPER WITH RELATIVE RETENTION TIME VALUES ON SE-30

| Compound*                 | Relative $R_F$ value |      | Relative retention time |       |
|---------------------------|----------------------|------|-------------------------|-------|
|                           | (a)                  | (b)  | (c)                     | (d)   |
| Fluorene                  | 4.00                 | 4.30 | 0.33                    | 0.28  |
| Anthracene                | 3.55                 | —    | 0.50                    | 0.457 |
| Phenanthrene              | 3.90                 | 4.78 | 0.50                    | 0.453 |
| Fluoranthrene             | 3.50                 | 4.73 | 0.88                    | 0.87  |
| Pyrene                    | 3.35                 | 5.03 | 1.00                    | 1.00  |
| Benzo(a)fluorene          | 2.35                 | —    | 1.16                    | 1.21  |
| Benzo(b)fluorene          | 2.45                 | —    | 1.19                    | 1.25  |
| Benzo(c)fluorene          | 2.65                 | —    | 1.19                    | 1.26  |
| Benzo(g,h,i)fluoranthrene | 3.20                 | —    | 1.68                    | 1.84  |
| Benzo(c)phenanthrene      | 2.75                 | —    | **                      | **    |
| Benz(a)anthracene         | 2.30                 | 4.25 | 1.83                    | 2.07  |
| Triphenylene              | —                    | 5.37 | 1.82                    | 2.07  |
| Chrysene                  | 1.50                 | 2.21 | 1.83                    | 2.08  |
| Tetracene                 | —                    | —    | 1.95                    | 2.21  |
| Benzo(b)fluoranthrene     | 1.43                 | —    | **                      | 4.01  |
| Benzo(j)fluoranthrene     | 1.70                 | —    | **                      | **    |
| Benzo(h)fluoranthrene     | 1.95                 | —    | **                      | 4.04  |
| Benzo(e)pyrene            | 2.70                 | —    | 3.64                    | 4.58  |
| Benzo(a)pyrene            | 1.00                 | 1.00 | 3.74                    | 4.72  |
| Perylene                  | 2.85                 | 3.76 | 3.85                    | 4.92  |
| Indeno(1,2,3-c,d)pyrene   | —                    | —    | **                      | 8.75  |
| Dibenz(a,h)anthracene     | 2.50                 | —    | 6.32                    | 8.96  |
| Benzo(c)tetraphene        | —                    | 1.80 | 6.54                    | 9.27  |
| Picene                    | —                    | 0.32 | 6.63                    | 9.31  |
| Dibenzo(a,c)phenanthrene  | 2.75                 | —    | **                      | **    |
| Benzo(g,h,i)perylene      | 3.35                 | —    | 7.11                    | 9.88  |
| Anthanthrene              | 1.20                 | 1.75 | 7.53                    | 10.50 |
| Coronene                  | 3.20                 | 4.40 | 13.5                    | —     |
| Dibenzo(a,h)pyrene        | 0.90                 | —    | **                      | **    |
| Dibenzo(a,i)pyrene        | 2.10                 | —    | **                      | **    |
| Dibenzo(a,l)pyrene        | 3.60                 | —    | **                      | **    |

(a) Acetylated cellulose, HOFFMANN AND WYNDER<sup>8</sup>.(b) Acetylated cellulose, SPOTSWOOD<sup>5</sup>.

(c) At 300° column temperature.

(d) At 260° column temperature.

\* The compounds bracketed together are unresolved by chromatography on SE-30 at an efficiency of  $10^4$  theoretical plates.

\*\* Relative retention time unknown.

The retention values differed only slightly whether determined on a kieselguhr-packed, a glass-bead-packed, or a capillary column (Tables I–V). There is, however, an unexplained discrepancy between certain of the values determined on the glass-bead column in this work and those reported by LIJINSKY *et al.*<sup>27</sup> (Table IV).

The use of capillary columns, and especially the 1 mm type which is useful for micro-preparative work, is a promising development and the overall time necessary for analysis of a polynuclear arene mixture can thereby be reduced considerably. A significant factor is the ease with which the capillary columns can be prepared. To utilize them to full advantage it will be necessary to study the problem of adsorption and means of overcoming it. The most likely method would seem to entail the use of a compact oxide-free metal rather than glass with its attendant disadvantages.



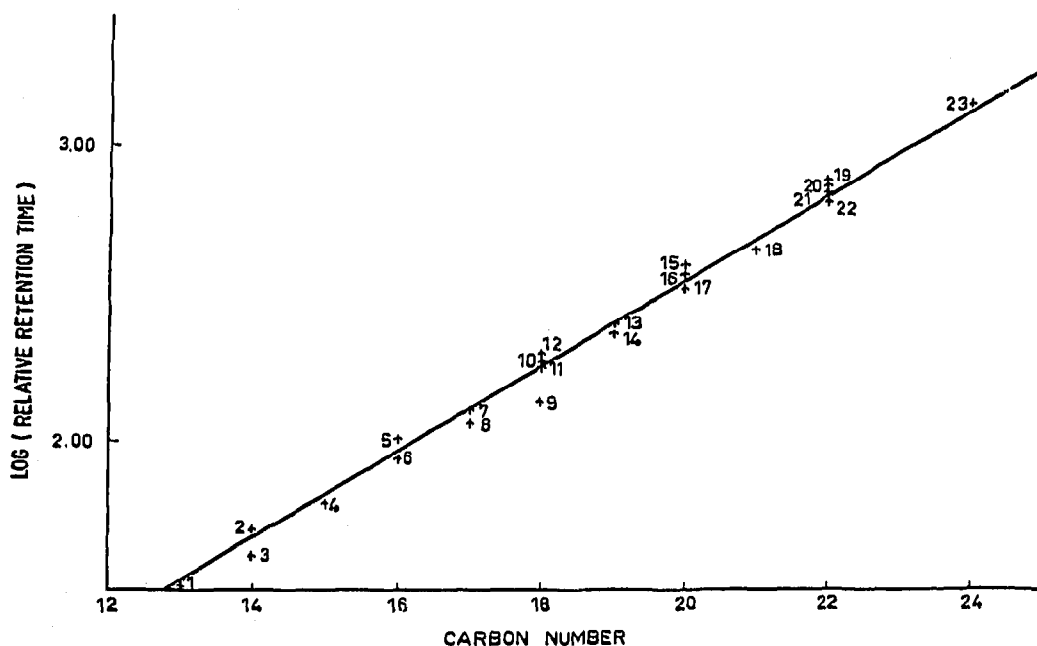


Fig. 1. Relation between relative retention time and carbon number. (1) fluorene; (2) phenanthrene; (3) 2-methylfluorene; (4) 3-methylphenanthrene; (5) pyrene; (6) fluoranthene; (7) 16,17-dihydro-15H-cyclopenta(*a*)phenanthrene; (8) benzo(*a*)fluorene; (9) 17-methyl-16,17-dihydro-15H-cyclopenta(*a*)phenanthrene; (10) chrysene; (11) benzo(*g,h,i*)fluoranthene; (12) naphthacene; (13) 2-methylchrysene; (14) 1-methylchrysene; (15) perylene; (16) benzo(*e*)pyrene; (17) benzo(*b*)fluoranthene; (18) 3-methylcholanthrene; (19) indeno(1,2,3-*c,d*)pyrene; (20) picene; (21) benzo(*g,h,i*)perylene; (22) anthanthrene; (23) coronene.

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#### SUMMARY

Gas chromatography has proved to be a convenient and rapid method for analysing mixtures of the polynuclear arenes. An analytical scheme is described for this analysis. Retention data are given for a number of these compounds on the phases SE-30, SE-52 and Q-F1. The use of packed and capillary columns has been investigated.

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