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# Gas chromatographic analysis of high-molecular-mass polycyclic aromatic hydrocarbons

## II. Polycyclic aromatic hydrocarbons with relative molecular masses exceeding 328

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ABSTRACT

Three columns were used for the gas chromatographic analysis of polycyclic aromatic hydrocarbons **(PAHs)** with relative molecular masses ($M_r$) up to 450. Two of the columns were commercially available, coated with a 50% methyltrifluoropropyl-substituted **polysiloxane** and a 5% diphenyl-substituted methylpolysiloxane. The third column was laboratory made, coated with a biphenyl-substituted **silarylene–siloxane** copolymer. All three columns were utilized for the analysis of high-$M_r$ **PAHs** as regards both thermal stability of the stationary phases, *i.e.*, low bleeding rate, and chromatographic efficiency. The column coated with a **trifluoropropyl-substituted** stationary phase showed, however, a low separation efficiency, possibly owing to low solute-stationary phase compatibility. The **biphenyl**-substituted stationary phase, on the other hand, showed a very high separation efficiency, but the retention of the **PAHs** was significantly higher on this column compared with the other two, leading to the demand for higher oven temperatures. **Different** retention mechanisms were observed on these columns, as shown by differences in the retention indices of the **PAHs** measured in a system using **PAHs** as retention index markers. A comparatively faster **elution** of non-planar **PAHs** was observed on the columns coated with the trifluoropropyl-substituted stationary phase and the biphenyl-substituted stationary phase compared with the column coated with the 5% diphenyl-substituted polymer. The usefulness of the columns for separations of **high-$M_r$ PAHs** is demonstrated by gas **chromatograms** of carbon black extracts and a coal tar extract standard reference material.

INTRODUCTION

Interest in the analysis of polycyclic aromatic hydrocarbons **(PAHs)** is mainly due to their **carcinogenicity** and/or mutagenicity. **PAHs** can be formed from incomplete combustion of fossil fuels and hence they are widespread in the environment. The group is large, with a large number of isomers, and this requires efficient separation methods in order to identify and determine individual PAH isomers. Focus has mostly been on analyses of **PAHs** having up to six aromatic rings. For this reason gas chromatography (GC) has become a useful method. For the analysis of higher relative molecular mass **($M_r$)** compounds, high-performance liquid chromatography (HPLC) has mostly been used **[1–7]**. However, some drawbacks are associated with this method, e.g., in ordinary HPLC the separation efficiency is often poor compared with GC and in micro-LC the analysis is often time consuming. A number of advantages can thus be gained if an efficient GC method for **high-$M_r$ PAHs** existed. In 1974 Grob **[8]** chromatographed rubrene **($M_r$** 532) on a 5.5-m capillary column. However, such short columns cannot

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be used for the separation of complex mixtures. In other investigations, carbon black samples were chromatographed and PAHs with molecular masses exceeding 300 were found [5,9,10]. Recently, a retention index system for PAHs having $M_r = 328$ was presented [11]. The isomers could be separated on a number of selected commercially and specially manufactured capillary columns with high temperature stability. In this study, the same chromatographic technique was used for the separation of PAHs with $M_r$ up to 450.

## EXPERIMENTAL

### *Columns*

Following a careful evaluation of more than ten different types of high-temperature-stable columns, three columns were chosen as suitable for GC of the high-$M_r$ PAHs. One of these was a stainless-steel column coated with a thin layer of fused silica and a methyltrifluoropropyl-substituted polysiloxane stationary phase, Rtx-200 (15 m × 0.28 mm I.D.; film thickness 0.10 $\mu$m). Second, a column coated with a methyl-5% diphenyl-substituted polysiloxane stationary phase was used. The tubing material, length, I.D. and film thickness were the same as for the Rtx-200 column. This column is denoted XTI-5. Those columns were obtained from Restek (Bellefonte, PA, USA). The third column (20 m × 0.32 mm I.D.) was prepared from polyimide-covered fused silica from Chrompack (Middelburg, Netherlands). This was coated with a biphenyl-substituted silarylene-siloxane copolymer synthezised at the University of Neuchatel (Neuchatel, Switzerland). The film thickness was only 0.05 pm. The columns were of the same types as in ref. 11, but in that instance the Rtx-200 and the XTI-5 columns had stationary phase film thicknesses of 0.25 pm.

### *Apparatus*

Chromatography was performed on a Carlo Erba (Milan, Italy) Mega gas chromatograph equipped with a flame ionization detector. A special high-temperature resistant detector tip made from polyimide was used. Hydrogen, passed through an oxygen trap, was used as the carrier gas. Signal recording and data handling were performed with an ELDS 900 laboratory data system (Chromatography Data System, Kungshög, Stenhamra, Sweden).

For the $M_r$ assessments of unknown samples, the columns were connected to an INCOS 50 quadrupole mass spectrometer (Finnigan MAT, San Jose, CA, USA) run in the electron impact (EI) mode. The gas chromatograph in that set-up was a Varian (Walnut Creek, CA, USA) Model 3400 and helium was used as the carrier gas. The columns were connected directly to the ion source. The transfer line temperature was kept at its maximum temperature of 350°C.

### *Solutes*

The structures of the compounds used for this evaluation are shown in Fig. la. The PAHs were all *peri*-condensed, with $M_r$ ranging from 352 to 426. In Fig. lb, the compounds used for retention index determinations are shown. Two standard series were evaluated: the picene standard series with picene, benzo[c]picene and dinaphtho[2,1-*a*:2,1-*h*)anthracene and the coronene standard series with coronene, benzo[a]coronene and dibenzo[*a,j*]coronene. All of the standard compounds were either purchased from Promchem (Wessel, Germany) or obtained from other laboratories (see Acknowledgements).

Apart from the pure standard compounds, two more complex samples were chromatographed. One of these was an HPLC fraction from standard reference material (SRM) 1597 (National Insitute of Standards and Technology), a coal tar extract [12] containing PAHs with $M_r$ exceeding 328. The other applications were two carbon black extracts: one dichloromethane extract and one chlorobenzene extract.

Chlorobenzene (BDH, Poole, UK) was used as the solvent for both the pure PAHs and the SRM and carbon black extracts.

### *Test conditions*

Hydrogen was used as the carrier gas and the inlet pressure was maintained so as to result in gas velocities of *ca.* 1.3 m/s at 140°C. On-column injections were performed in all instances. The oven temperature was kept at 140°C during injection. After a 2-min isothermal period, the oven temperature was increased at 30°C/min to 200°C and 4 min from the injection time the temperature programme was started at a rate of 5°C/min to different upper temperature levels. The Rtx-200 column was used up to

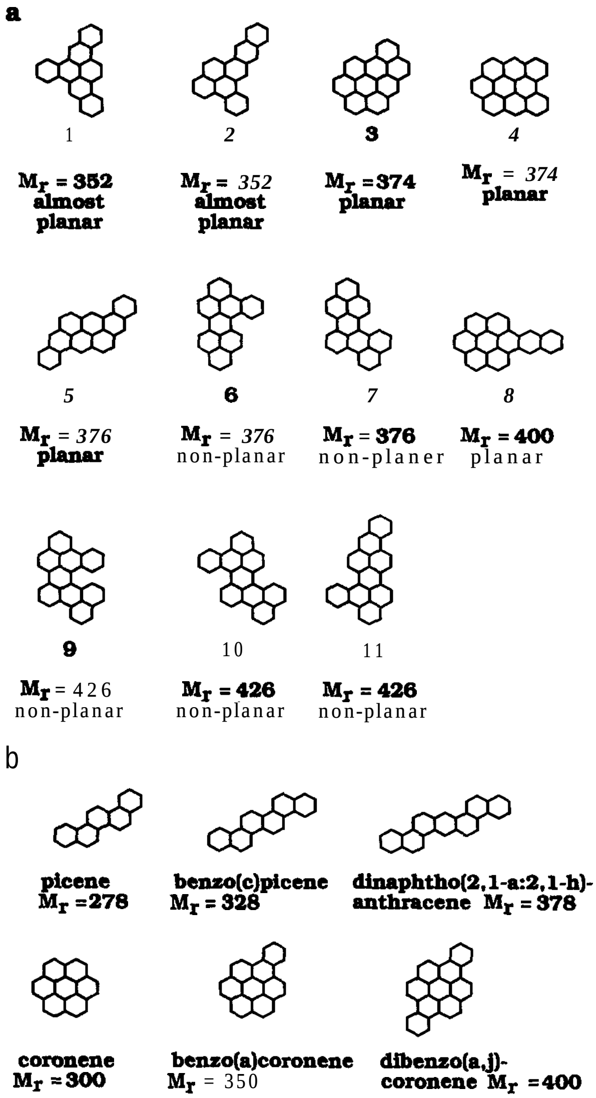

Fig. 1. Molecular structures of (a) peri-condensed PAHs and (b) retention index markers.

360°C, the XTI-5 column up to 380°C, and the silabiphenyl column up to 400°C. The upper temperature was dependent on the last-eluting compound, *i.e.*, all the standard compounds (Fig. 1) were forced to elute within the temperature programming ramp in order to obtain a temperature-programmed retention index for each compound.

The individual PAH components were diluted in chlorobenzene at concentrations resulting in constant retention times and symmetrical peaks independent of sample sizes injected. The injection volume was kept as small as possible and ranged from 0.2 to 1.0 $\mu$l.

### *Retention index determinations*

Temperature-programmed retention indices were measured according to Lee *et al.* [13], *i.e.*, by linear interpolation between two PAH index markers adjacent to the compound to be measured. In the picene standard series, picene was given the value of 500, benzo[*c*]picene 600 and dinaphtho[2,1-*a*:2,1-*h*]anthracene 700. In the coronene standard series, coronene was given a value of 100, benzo[*a*]coronene 200 and dibenzo[*a,j*]coronene 300. For all compounds eluting after the last retention index marker in each system, the retention index values were extrapolated. For comparison, in one example retention indices were calculated with *n*-alkane homologues ranging from $C_{15}$ to $C_{34}$ according to ref. 14.

## RESULTS AND DISCUSSION

### *Columns*

In a previous study, PAHs of $M_r$ 328 were subjected to GC [11]. After careful evaluation of the available columns and stationary phases, four columns were found suitable in that work. However, for higher $M_r$, those columns were found not to be useful owing to high retention times. However, this could be overcome by using columns with decreased film thicknesses. In this work, the Rtx-200 and XTI-5 types of columns were used with film thicknesses of 0.10 $\mu$m. For the silabiphenyl column the elution temperature was decreased by means of an increased inlet pressure, *i.e.*, from 0.5 to 0.9 bar. As was observed previously [11], the trifluoropropyl-substituted stationary phase exhibited low retentions for the high-M, PAHs. From the peak shapes it was concluded that the low retention mainly was due to low solubility of the high-M, PAHs in the stationary phase. This was also experienced in this work. In Fig. 2, chromatograms of a mixture of the *peri*-condensed PAHs injected together with the retention index markers are shown. In Fig. 2a, the chromatogram obtained from the XTI-5 column shows that two of the highest-M, compounds ($M_r$ 426) were eluted at 360°C. On the Rtx-200 column in Fig. 2b, the elution temperature for these com-

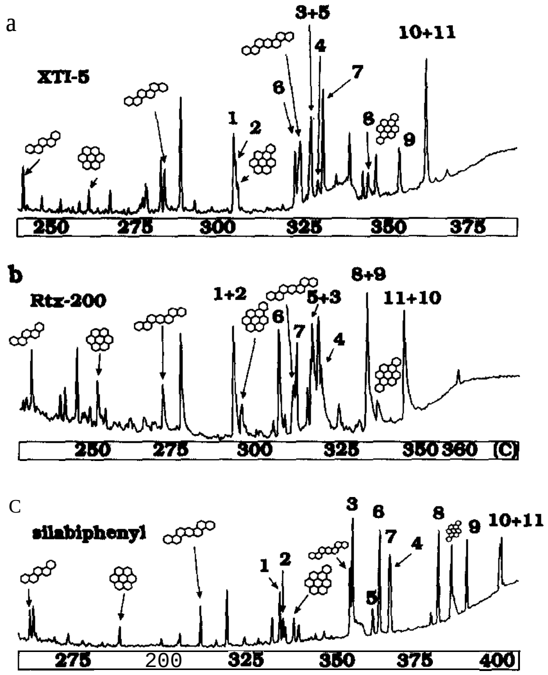

Fig. 2. Gas chromatograms with flame ionization detection (FID) of per&condensed PAHs on (a) the XTI-5, (b) the Rtx-200 and (c) the silabiphenyl column. Conditions: on-column injection at 140°C, after a 2-min isothermal period heated at 30°C/min to 200°C and after 4 min from the injection programmed at 5°C/min to (a) 380°C, (b) 360°C and (c) 400°C. Peak numbers refer to Fig. la.

pounds was below 350°C. The column dimensions, film thicknesses, inlet pressures and temperature programming rate were identical for these two columns. In Fig. 2c, the chromatogram of the same mixtures obtained on the silabiphenyl column shows that the elution temperature of the two last eluting compounds was almost 400°C. A valuable observation is that the silabiphenyl column was able to separate slightly the two last-eluting isomers of $M_r$ 426.

Column efficiency can be measured in terms of Trennzahl numbers when temperature-programmed runs are considered. The Trennzahl numbers for coronene-benzo[a]coronene were 35, 58 and 76 for the Rtx-200, XTT-5 and silabiphenyl columns, respectively. For all columns, the separation numbers were slightly higher for theperi-condensed types of PAHs, *i.e.*, coronene-benzo[a]coronene, than for the linear (*cata*-condensed) types of PAHs (benzo[*c*]picene–dinaphtho[2,1-*a*:2,1-*h*)anthracene).

*Retention indices*

Commonly used markers for retention index assessments are a homologous series of n-alkanes. However, the advantage of employing retention index markers similar to the compounds to be measured has been pointed out earlier concerning both isothermal [15] and temperature-programmed runs [13,14]. Dissimilar markers and compounds to be measured will have different partition coefficients at different temperatures, which can result in temperature-dependent retention indices and even changes in elution order [16]. A consequence of this is that when using an *n*-alkane homologous series as retention index markers for PAHs, the retention indices will be dependent on elution temperature. Table I shows a comparison between retention indices obtained by use of an *n*-alkane standard series and the

TABLE I

COMPARISON OF INDICES IN THE PICENE STANDARD SERIES AND THE *n*-ALKANE SERIES OBTAINED ON THE SILABIPHENYL COLUMN OPERATED AT DIFFERENT INLET PRESSURES (12–15°C DIFFERENCE IN ELUTION TEMPERATURE)

| Compound | *n*-Alkane standard | | | Picene standard | | |
|---|---|---|---|---|---|---|
| | $P_i$ = 55 | $P_i$ = 90 | AA | $P_i$ = 55 | $P_i$ = 90 | AP |
| Chrysene | 2836 | 2819 | 17 | 400 | 400 | – |
| Benzo[e]pyrene | 3314 | 3276 | 38 | 454.4 | 454.1 | 0.3 |
| Picene | 3765 | 3685 | 80 | 500 | 500 | – |
| Coronene | 4288 | 4183 | 105 | 553.2 | 554.3 | – 1.1 |
| Benzo[*c*]picene | 4747 | 4637 | 110 | 600 | 600 | – |
| Benzo[*a*]coronene | 5348 | 5213 | 135 | 662.5 | 663.1 | -0.6 |

TABLE II

TEMPERATURE-PROGRAMMED AVERAGE RETENTION INDICES OF THE PER&CONDENSED **PAHs** MEASURED WITH THE PICENE STANDARD SYSTEM

| Compound” | I ± S.D | | |
|---|---|---|---|
| | XTI-5 | Rtx-200 | Silabiphenyl |
| **Picene** | **500** | 500 | 500 |
| Coronene | 546.41 ± 0.07’ | 549.57 ± 0.43[d] | 552.69 ± 0.06’ |
| Benzo[c]picene | 600 | 600 | 600 |
| 1 | 651.93 | 653.20 | 653.01 |
| *2* | 653.44 | 656.15 | 655.00 |
| Benzo[a]coronene | 654.77 ± 0.21’ | 660.02 ± 0.37” | 662.36 ± 0.14’ |
| 6 | 697.73 | 688.32 | 701.59 |
| **Dinaphtho[2,1-*a*:2,1-*h*)anthracene** | 700 | 700 | 700 |
| **3**[b] | 708.80 | 715.48 | 719.50 |
| **5**[b] | 709.55 | 715.19 | 714.86 |
| **4**[b] | 714.66 | 721.18 | 727.01 |
| **7**[b] | 718.81 | 703.50 | 726.15 |
| **8**[b] | 752.57 | 756.85 | 758.99 |
| **Dibenzo[*a,j*]coronene**[b] | 758.47 ± l.W | 765.36 ± 1.46“ | 767.32 ± 0.34’ |
| **9**[b] | 775.90 | 756.26 | 777.56 |
| lob | 795.35 | 785.48 | 799.54 |
| **11**[b] | 796.35 | 784.97 | 800.78 |

[a] Numbers refer to compounds in Fig. la.

[b] Extrapolated values from **benzo[*c*]picene–dinaphtho[2,1-*a*:2,1** -h]anthracene.

[c] Fourteen determinations.

[d] Eleven determinations.

[e] Twelve determinations.

[f] Thirteen determinations.

picene standard series. The column used was **sila**biphenyl at two different inlet pressures, 0.5 and 0.9 bar. This pressure difference resulted in a cu. 15°C lower elution temperature for the higher inlet pressure, 0.9 bar. Some lower-M, **PAHs** were added to this mixture, i.e., chrysene and benzo[e]pyrene. The temperature programming, at **7°C/min,** was started 2 min from injection, which was performed at 70°C. Differences in the n-alkane system, denoted $\Delta A$, show that the n-alkane retention index differences will increase during the temperature-programmed run. On the other hand, the retention indices measured with the picene standard system remain fairly constant ($\Delta P$). The absolute figures also reflect the fact that the PAH retention index system is much more insensitive to changes in elution temperature. However, it should be kept in mind that 1 index unit in the PAH system is comparable to 10 units in the n-alkane system, although the accuracy of the PAH retention index system is superior to the n-alkane system when applied to **PAHs.**

Based on the above discussion, it was of interest to compare retention indices observed on different columns. If the forces acting on the retention index markers and the solutes are similar, similar retention indices should be obtained independent of the stationary phase properties. The retention indices for the p&-condensed **PAHs** in the picene standard system are listed in Table II and in the coronene standard system in Table III. It can be seen that the retention indices for some compounds differ considerably between columns.

As shown in an earlier study **[11],** differences in the retention indices of **PAHs** were observed when comparing different columns. Deviations could be referred to differences in planarity. This was also found to be true for the higher-M, **PAHs** (Tables II and III). A comparatively lower retention for the

TABLE III

TEMPERATURE-PROGRAMMED AVERAGE RETENTION INDICES OF THE PER&CONDENSED **PAHs** MEASURED WITH THE CORONENE STANDARD SYSTEM

| Compound | I ± S.D | | |
|---|---|---|---|
| | XTI-5 | Rtx-200 | Silabiphenyl |
| Picene[b] | 55.83 ± 0.07’ | 55.36 ± 0.96“ | 48.32 ± 0.17’ |
| Coronene | 100 | 100 | 100 |
| Benzo[c]picene | 150.97 ± 0.09’ | 145.63 ± 0.56’ | 146.41 ± 0.10” |
| 1 | 197.47 | 193.79 | 192.00 |
| 2 | 198.70 | 196.37 | 193.72 |
| Benzo[a]coronene | 200 | 200 | 200 |
| 6 | 241.37 | 226.15 | 237.48 |
| Dinaphto[2,1-*a*:2,1-*h*]anthracene | 243.54 ± 0.39’ | 237.83 ± 0.94’ | 235.82 ± 0.13’ |
| 3 | 252.26 | 252.98 | 254.72 |
| **5** | 252.66 | 251.89 | 250.14 |
| 4 | 257.86 | 258.65 | 261.48 |
| **7** | 261.86 | 240.88 | 260.79 |
| **8** | 294.83 | 292.16 | 291.88 |
| Dibenzo[*a,j*]coronene | 300 | 300 | 300 |
| **9**[f] | 315.99 | 290.66 | 309.96 |
| **10**[f] | 335.40 | 318.14 | 330.94 |
| **11**[f] | 335.90 | 317.54 | 331.90 |

[a] Numbers refer to compounds in Fig. la.

[b] Extrapolated value from coronene–benzo[*a*]coronene.

[c] Thirteen determinations.

[d] Eleven determinations.

[e] Twelve determinations.

[f] Extrapolated values from benzo[*a*]coronene–dibenzo[*a,j*]coronene.

non-planar **PAHs** was observed on the Rtx-200 column (Fig. 2b), where, e.g., compound 9 elutes prior to dibenzo[*a,j*]coronene. Further, both the non-planar compounds 6 and 7 elute before the planar compounds 3, 4 and 5 on this column. The differences in retention indices (*ΔI*) between the Rtx-200 and the XTI-5 columns (expressed as $I_{\mathrm{Rtx\text{-}200}} - I_{\mathrm{XTI\text{-}5}}$) are shown in Fig. 3. The retention indices were measured with the coronene standard system. Large deviations were observed for the non-planar **PAHs** (black bars in Fig. 3). Retention differences with up to 25 index units were observed. For the planar and almost planar compounds, the difference in no case exceeded 5 index units. If the same comparison is made for the silabiphenyl column and the XTI-5 column (Fig. 4), the result is not so evident. The absolute differences in retention indices (*ΔI*) between the silabiphenyl and XTI-5 column never exceeded 8 index units. However, a decreased retention for the non-planar **PAHs** can also be observed on this column. This can be seen from, e.g., the last three compounds, 9, 10 and 11, having $M_r$ 426, which are all non-planar. The increased retention of the planar **PAHs** is probably greater for this column, e.g. compounds 3 and 4. An attempt to correlate the retention indices with polarizability and connectivity [17] could not easily explain the behaviour for the silabiphenyl column, but probably a complex charge-transfer interaction between the biphenyl units and the **PAHs** is involved, in addition to other shape parameters apart from planarity.

### *Applications*

A fraction of SRM 1597, a coal tar extract, previously fractionated by HPLC was injected on to the XTI-5 and silabiphenyl columns together with the retention index markers. This fraction should contain **PAHs** of $M_r > 328$. In previous work [11], the fraction having $M_r$ 328 was analysed in a similar

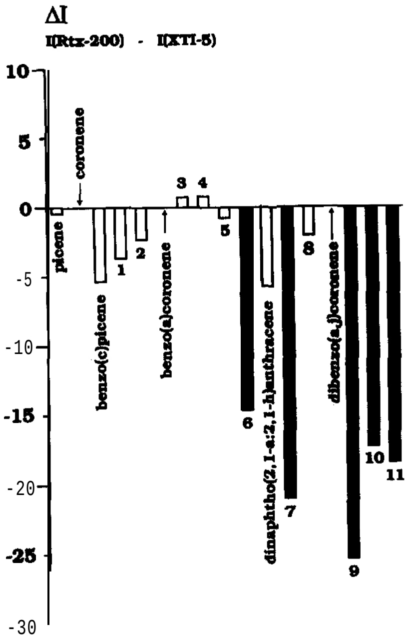

Fig. *3*. Absolute differenccs in retention indices, *AI*, between the Rtx-200 and the XTI-5 columns, measured with the coronene standard system. Black bars indicate non-planar compounds. Numbers refer to the compounds in Fig. la.

manner and then found to be a mixture of PAHs having $M_r$ 326 and 328. In Fig. 5, the chromatograms of the fraction having $M_r > 328$ obtained on (a) the XTI-5 and (b) the silabiphenyl columns are shown. From mass spectrometric measurements, it was concluded that this fraction mainly contained PAHs having $M_r$ 352 and a few compounds with $M_r$ 374 and 376.

As a second application, a dichloromethane and a chlorobenzene extract of a carbon black sample were chromatographed. In Fig. 6, the chromatograms obtained on the XTI-5 column are shown. The ability to resolve the higher-M, compounds was limited for this column, but owing to the comparatively low elution temperature (380°C) it was possible to identify the individual masses in the different fractions by mass spectrometry. The group eluting after dibenzo[*a,j*]coronene consisted mainly of PAHs having $M_r$ 424 and a few with $M_r$ 426. The next group consisted mainly of PAHs having $M_r$ 448 and a few compounds with $M_r$ 450. The last-eluting group contained mainly PAHs with $M_r$ 472.

In Fig. 7, the same fractions were chromatographed on the silabiphenyl column. The elution temperature for the last-eluting groups was 400°C. On connecting the column to the mass spectrometer, these compounds were trapped within the last section of the column in the transfer line, which was temperature limited to 350°C. The last compound identified by GC-MS was ovalene, having $M_r$ 398. The masses indicated in the chromatogram in Fig. 7 were tentatively identified by guidance from the MS data obtained from the XTI-5 column (Fig. 6). However, the silabiphenyl column demonstrates a marked separation efficiency even at temperatures up to 400°C.

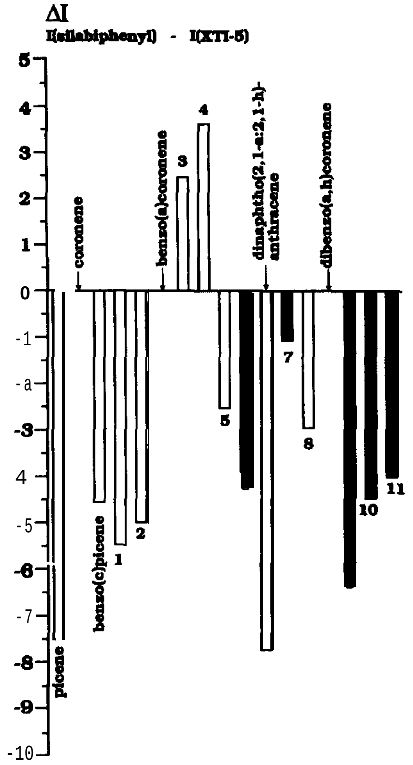

Fig. 4. Absolute differences in retention indices, *AI*, between the silabiphenyl and the XTI-5 columns, measured with the coronene standard system. Black bars indicate non-planar compounds. Numbers refer to the compounds in Fig. la.

## CONCLUSIONS

The results clearly demonstrate that comparably high-$M_r$ PAHs can be separated and identified by using GC. A few commercial columns are already

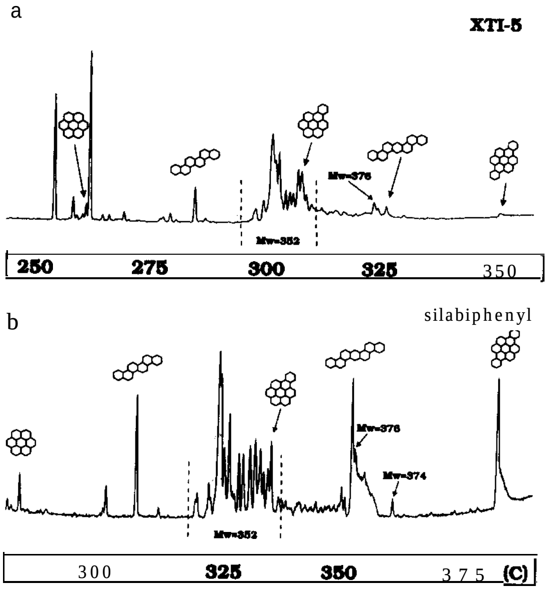

Fig. 5. Gas chromatograms (FID) of SRM 1597, an HPLC fraction having $M_r > 328$, injected together with the retention index markers on (a) the XTI-5 and (b) the silabiphenyl column. Temperature programming as in Fig. 2.

available that can be used successfully in the separation process. It is hoped that other high-temperature stable stationary phases such as the biphenyl-based material described here will become available.

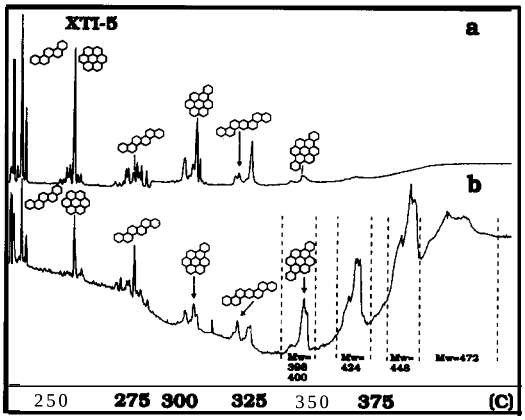

Fig. 6. Gas chromatograms (FID) of (a) a dichloromethane extract and (b) a chlorobenzene extract of carbon black on the XTI-5 column. Temperature programming as in Fig. 2. The indicated mass numbers were identified by CC-MS.

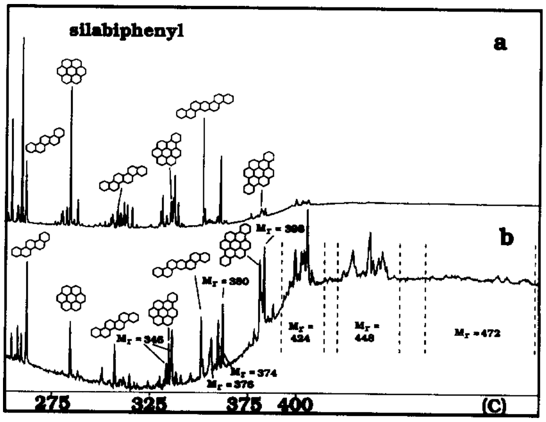

Fig. 7. Gas chromatograms (FID) of (a) a dichloromethane extract and (b) a chlorobenzene extract of carbon black on the silabiphenyl column. Temperature programming as in Fig. 2. The indicated mass numbers >400 were tentatively identified by guidance from the CC-MS data obtained from the XTI-5 column.

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