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Gas chromatographic analysis of high-molecular-weight polynuclear aromatic hydrocarbons

I. Molecular weight 328

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ABSTRACT

Various columns were investigated with respect to the gas chromatographic analysis of polynuclear aromatic hydrocarbons (PAHs) having molecular weights that exceed 300. Among the columns tested, four columns differing in stationary phase composition were carefully evaluated. Three of these columns were commercially available. The evaluation was focused on cata-condensed PAHs of molecular weight 328. Temperature-programmed retention indices with PAHs as reference markers were calculated and compared.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are hazardous environmental chemicals. They are formed primarily during incomplete combustion or pyrolysis of organic materials. The PAH group contains the largest number of mutagenic and/or carcinogenic substances [1,2]. High-molecular-weight PAHs, with six or more rings, are not a well studied group, but their carcinogenic properties are anticipated [3]. Some of these PAHs have been confirmed to be inactive, whereas others have shown weak or moderate activity [4]. Owing to difficulties in the analysis of these compounds, little information on their ambient levels is available. However, some studies have been made. For example, Fetzer and co-workers [5,6] analysed a sample of diesel engine particulate matter and confirmed the existence of naphtho[8,1,2-*abc*]coronene with a molecular weight (M_W) of 374. All PAHs having six or more rings were found to be highly fused types, *i.e.*, no linear or non-alternant PAHs were seen in that sample. The same results were obtained by Peaden

et al. [7], who separated a carbon black extract by high-performance liquid chromatography (HPLC) and made molecular weight assessments by use of mass spectrometry (MS). They did not find any PAHs of MW = 328 (cata-condensed types) within that sample. However, some sompounds with five-membered rings were found. Romanowski *et al.* [8] reported the existence of PAHs with molecular weights exceeding 300 in an airborne particulate matter. No identifications were made but the sample was analysed by gas chromatography (GC)–MS, showing some compounds with a molecular weight of 328.

For the separation of complex mixtures, capillary GC is a powerful technique owing to its high resolving power. However, for the chromatography of high-molecular-weight compounds, the elution temperature may exceed the temperature limit of the capillary column. The maximum allowable temperature for a capillary column is determined by the temperature stability of the stationary phase and the capillary material.

In recent years, interest in producing heat-stable

stationary phases has increased. Both the common phases, *i.e.*, methylsilicone and methylphenylsilicone types, and newer modified phases such as the siloxane/silarylene phases [9,10], carborane-modified types [11,12] and polysulphone-modified silicone stationary phases [13,14], have been refined to meet the increased demands on thermal stability.

The temperature limit of a capillary column is also determined by the capillary material. Polyimide-clad fused-silica columns have become commonly used. A serious drawback, however, is the temperature limit of the polyimide, *viz.*, *ca.* 370°C. Even though the column could be used for a short time above this temperature, the lifetime will drastically decrease. To overcome this problem, Lipsky and Duffy [15,16], introduced alumina-clad fused-silica capillaries which were claimed to withstand temperatures far above the polyimide-clad capillary limit. Good elution of, *e.g.*, triglycerides on these columns has been reported [15–17]. The maximum temperature was 440°C. However, in our experience, columns prepared with this type of capillary material become even more brittle than the polyimide-clad columns after high-temperature exposure for an extended period of time.

Another type of high-temperature columns evaluated are the metal capillaries [18,19] recently reintroduced by Chrompack. The material can withstand temperatures above 500°C. In 1987, Termonia *et al.* [20] described high-temperature GC by use of a stainless-steel-armoured polyimide-clad fused-silica column (Rescom, Belgium). Restek have developed stainless-steel columns to which is bound a layer of fused silica a few micrometres thick (Silcosteel) [21].

Inexpensive and durable columns can be made from borosilicate glass. Columns prepared from this material were suggested by Rohwer and Pretorius [22]. It has also successfully been used by Blum and co-workers in the preparation of high-temperature stable, medium-polarity columns used for the analysis of antioxidants, UV stabilizers [23] and metalloporphyrins [24,25].

For the analysis of high-molecular-weight PAHs, the method of choice has been reversed-phase LC [5–7, 26–28], in some instances with the use of packed capillary LC columns [26,27]. The main reason for not analysing these substances by GC lies in their low vapour pressure and low stationary phase solubility. However, a few attempts have been made to chromatograph PAHs of molecular weight exceeding 300 by GC. In 1974, Grob [29] presented a method to chromatograph rubrene (MW 532). The column was only 5.5 m long and the oven temperature was programmed up to 260°C. However, such short columns cannot be used for the separation of complex mixtures. Carbon black samples have been analysed by GC using non-polar, commercially available capillary columns [8,26] and on a laboratory-made medium-polarity column [30] (methylphenylpolysiloxane having 70% phenyl substitution). Peak asymmetry of late-eluting components was reported [26], which was claimed to be attributed to the low solubility to the high-molecular-weight PAHs in the methylpolysiloxane stationary phase. This conclusion indicates the need for columns having stationary phases with higher polarizability to facilitate dissolution of these particular compounds. However, better dissolution means increased retention, requiring increased oven temperatures.

The aim of this work was to evaluate columns with respect to the GC analysis of PAHs of molecular weight 328.

EXPERIMENTAL

Columns

Four different columns were evaluated. The first column was a thin-film (0.12 μm) CP-Sil 8 (having 5% phenyl substitution) polyimide-protected fused-silica column (25 m × 0.32 mm I.D.) from Chrompack (Middelburg, Netherlands). Further, two stainless-steel columns (15 m × 0.28 mm I.D. with a film a few micrometres thick of fused-silica bound to the metal, obtained from Restek (Bellefonte, PA, USA) were tested. One was coated with a methyltrifluoropropylpolysiloxane stationary phase, Rtx-200, and the other with a methyldiphenylpolysiloxane having 5% diphenyl substitution, XTI-5. Both had a film thickness of 0.25 μm and were immobilized. Finally, one laboratory made column was evaluated. The stationary phase was a silarylene/siloxane copolymer having 25% biphenyl substitution, synthesized at the University of Neuchatel, Switzerland. The polymer was coated on polyimide-protected fused-silica tubing (Chrompack) which was flushed with nitrogen prior to the static

coating. The coating procedure was described in a previous paper [10].

Apparatus

GC was performed on a Carlo Erba (Milan, Italy) Model 4160 gas chromatograph equipped with a flame ionization detector. The chromatograph was connected to a laboratory data system (ELDS 900; Chromatography Data Systems, Kungshög, Stenhamra, Sweden). All recording and calculations of chromatographic data were performed with this system. Hydrogen, passed through an oxygen trap, was used as the carrier gas.

For comparison, som experiments were made on a Hewlett-Packard (Avondale, PA, USA) Model 5790 gas chromatograph equipped with a flame ionization detector and connected to the same laboratory data system as above. The carrier gas was oxygen-free helium.

Solutes

The PAHs studied were either commercially available (Promochem, Wessel, Germany) or obtained from other laboratories (see Acknowledgements). There are 39 possible PAH isomers with a molecular weight of 328 containing six fused benzene rings. In this work 14 of these isomers were studied (Fig. 1). The compounds were dissolved in chlorobenzene (BDH, Poole, UK).

To be able to compare the retention indices obtained on the columns evaluated with those published by Lee *et al.* [31], a standard mixture containing seventeen lower molecular weight PAHs, ranging from phenanthrene to coronene, dissolved in cyclohexane–acetone (1:1) was analysed. The larger standard compounds, *viz.*, benzo[c]picene, dinaphtho[2,1-a:2,1-h]anthracene and benzo[a]coronene, were also included in this mixture.

As an application of the utility of the columns, an HPLC fraction NBS Standard Reference Material (SRM) 1597, a coal tar extract, [32] containing PAHs with molecular weight 328, dissolved in chlorobenzene, was analysed.

Test conditions

All injections were performed in the on-column mode, except for determinations of capacity factors (k') and column efficieny [measured as height equivalent to a theoretical plate (HETP)], where the split
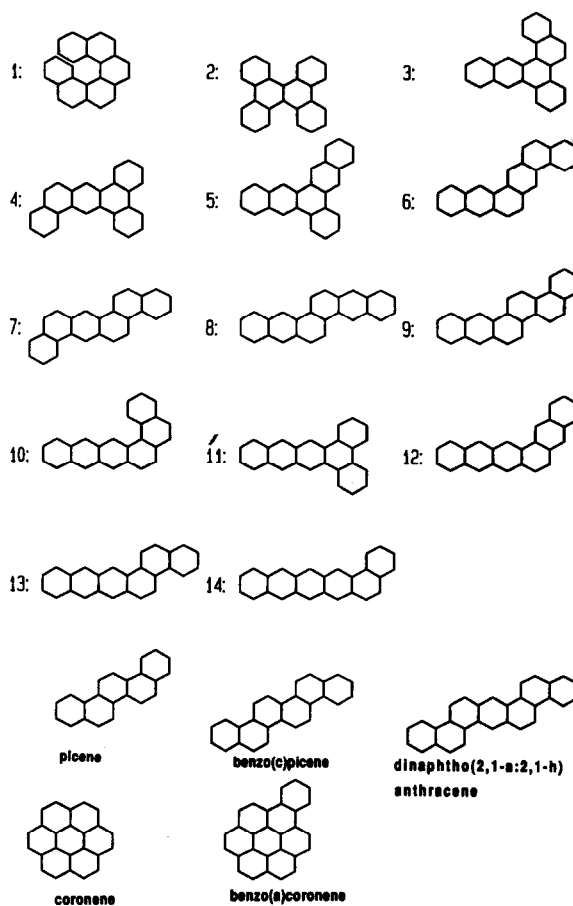

Fig. 1. Structures of the cata-condensed PAHs of molecular weight 328 used in these experiments and the structures of the compounds in the two standard series. All rings are aromatic.

mode was used. In the split mode, the injector temperature was kept at 320°C and the oven temperature was 300°C. The detector temperature was held at 400°C during all runs, except with the Rtx-200 column, where it was 370°C. In the split mode, 1.0 μl of coronene in chlorobenzene was injected with a spliting ratio of 1:200.

For the PAHs in Fig. 1 (MW 328), introduced in the on-column mode, the oven temperature was held at 140°C during the injection. After a 2-min isothermal period, the oven was rapidly heated to 200°C, and after 4 min from injection the temperature programming was started at a rate of 5°C min to 350 or 370°C. The inlet pressure was set to give a slightly higher gas velocity than the optimum (mea-

sured at 300°C). The inlet overpressure ranged from 0.5 to 0.7 atm depending on the length and I.D. of the columns. The injection volume ranged from 0.2 to 1.0 μl per injection.

The PAH mixture containing lower-molecular-weight compounds was also introduced in the on-column mode. The injection volume was 1.0 μl injected at 70°C; after a 2-min isothermal period the oven was programmed at a rate of 5 or 7°C min to 350 or 370°C.

Retention index determinations

The temperature-programmed retention indices (RI) were determined according to the model described by Lee *et al.* [31], where phenanthrene, chrysene, picene and benzo[*c*]picene were used as standard compounds. We found it necessary to extend this standard series by introduction of dinaphtho[2,1-*a*:2,1-*h*]anthracene as the last-eluting standard compound. The addition of this compound is not consistent with the remainder of the series. This is a compromise owing to a lack of the correct standard substance. For the retention index determinations, the value for phenanthrene was set at 300, chrysene at 400, picene at 500, benzo[*c*]picene at 600 and dinaphtho[2,1-*a*:2,1-*h*]anthracene at 700. As an alternative series, a standard series with coronene and benzo[*a*]coronene was used, where coronene was given the value of 100 and benzo[*a*]coronene 200. Molecular structures of the standard series of compounds are shown in Fig. 1. The retention index values for the PAHs investigated were obtained by linear interpolation between the standard compounds eluting just before and after the compound to be determined.

RESULTS AND DISCUSSION

This work was focused on temperature-programmed retention index assessments of some cata-condensed PAH isomers consisting of six fused benzene rings (MW 328) (Fig. 1). The indices were measured in two different standard systems and calculated according to ref. 31. One series consisted of phenanthrene, chrysene, picene, benzo[*c*]picene and dinaphtho[2,1-*a*:2,1-*h*]anthracene and the other series coronene and benzo[*a*]coronene. Ten commercially available columns from five different manufacturers were tested, but only a few were sufficient-

ly stable with regard to both the capillary material and the stationary phase stability.

Owing to the low vapour pressure and high boiling points for the high-molecular-weight PAHs, a column intended for the GC analysis of these compounds must be stable at high temperatures, hence a stable stationary phase and a stable protecting layer are required. However, the stationary phase must not only be heat stable, it must also maintain good chromatographic properties at elevated temperatures. When high-molecular-weight compounds are considered in GC, columns having thin stationary phase films are preferred from the viewpoint of elution temperature. The drawback with such columns is a low solute capacity. Moreover, it is favourable if the stationary phase interacts only weakly with the compounds to be chromatographed, giving a comparatively lower elution temperature. Considering the latter fact, a pure methylsilicone stationary phase should be a good choice. However, the solubility of the high-molecular-weight PAHs in these phases is low [26]. The optimum column for the GC of high-molecular-weight PAHs should exhibit solute solubility combined with good thermal stability with low bleeding profiles. As will be discussed, all these criteria are difficult to fulfil, but compromises are possible.

Columns

Among the columns examined, the stainless-steel fused-silica capillary column coated with a methyltrifluoropropyl stationary phase, Rtx-200, was the most non-polar or exhibited the lowest interaction between the stationary phase and the solutes. In Table I are listed the column properties, including the k' values at 300°C for coronene, the corresponding HETP values, the β-value (gas to liquid volume ratio) and the partition coefficient, K, at 300°C (calculated as $\beta k'$), which describes the solute solubility or the magnitude of interaction between the stationary phase and the solute. As shown in Table I, the Rtx-200 column has the lowest K value but also a low column efficiency. According to the peak shapes observed for the high-molecular-weight PAHs on this column, the low efficiency seems to depend mainly on a low compatibility between, *e.g.*, coronene and the non-polar stationary phase. On the other hand, the low retention on this stationary phase made it possible to elute the highest molec-

TABLE I

COLUMN CHARACTERISTICS AND CHROMATOGRAPHIC PROPERTIES OF CORONENE AT 300°C

Column	Length (m)	I.D. (mm)	k' (300°C)	HETP (mm)	β	K (300°C)
Rtx-200	15	0.28	5.88	0.43	280	1646
CP-Sil 8	25	0.32	3.40	0.32	667	2268
XTI-5	15	0.28	8.83	0.35	280	2472
Silabiphenyl	20	0.32	6.93	0.34	1600	11086

ular weight compound examined below 330°C, i.e., dinaphtho[2,1-a:2,1-h]anthracene (MW 378).

Next in order of polarity are the polyimide-covered fused-silica column, CP-Si 8, with a chemical composition of 5% phenyl and 95% methyl substitution, and the stainless-steel fused-silica column,

XTI-5, with 5% diphenyl substitution. Owing to the similarity of their stationary phases they exhibit similar retention properties. These columns had K values that were ca. 33% higher than that for the Rtx-200 column, indicating increased interactions between the stationary phases and the solute.
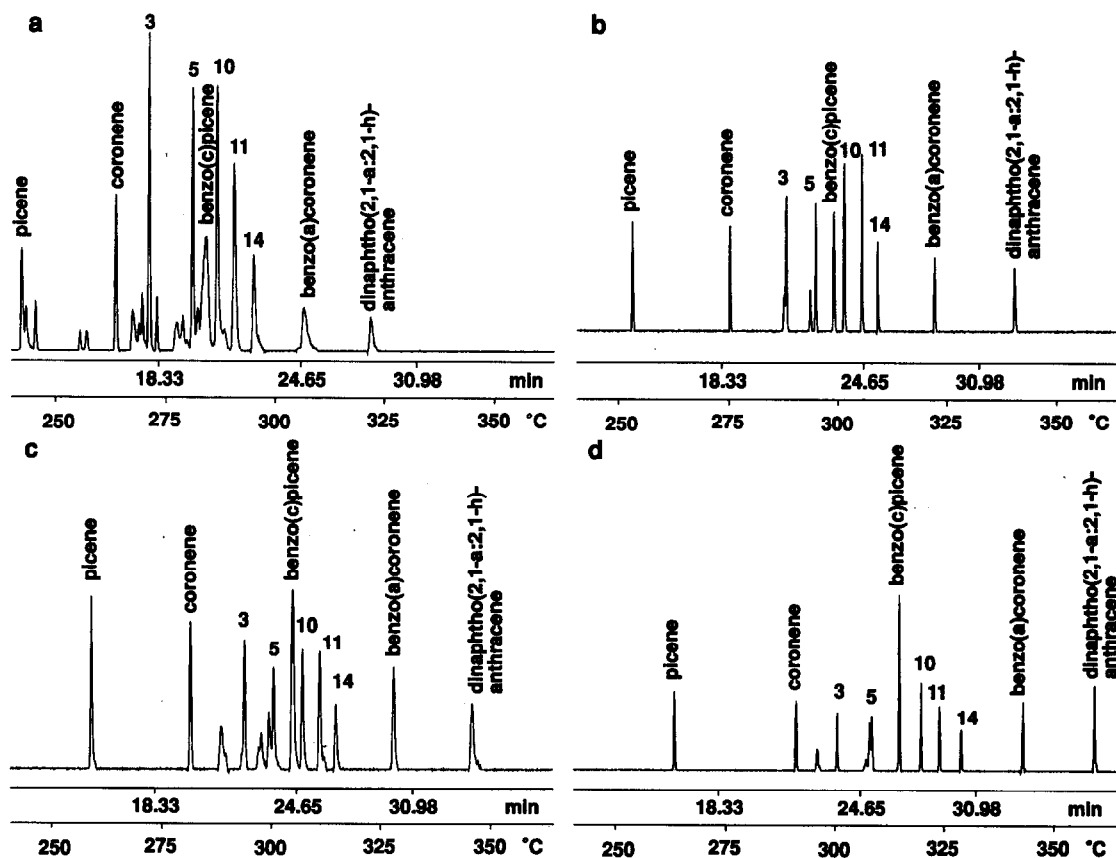

Fig. 2. Baseline-substracted gas chromatograms (flame ionization detection) of a PAH mixture on (a) the Rtx-200 column, (b) the CP-Sil 8 column, (c) the XTI-5 column and (d) the silabiphenyl column. Conditions: on-column injection at 140°C, after 2 min rapidly heated to 200°C and after 4 min from time of injection programmed at 5°C/min to (a) 350°C and (b–d) 370°C. Peak numbers refer to the compounds in Fig. 1.

For the silabiphenyl column, comparison of the partition coefficient in Table I shows very high interactions between the stationary phase and coronene. This non-commercially available column cannot be used for chromatography below 150°C.

In Fig. 2 are shown some chromatograms obtained with these columns. The peak numbers refer to the compounds in Fig. 1. All the chromatograms are baseline subtracted, making it easier to compare the peak shapes and resolution. The CP-Sil 8 and silabiphenyl columns show the best eluition patterns. These two columns were coated with the thinnest stationary phase films, i.e., 0.12 and 0.05 μm. Owing to increased resistance to mass transfer in the liquid phase, it is not completely possible to compare columns with thick and thin stationary phase films with regard to the column efficieny.

In Fig. 3 are shown runs made with the same temperature programmmes to show the bleeding profile on these columns. A high bleeding rate was observed for the CP-Sil 8 column at increased temperatures, whereas the XTI-5 and silabiphenyl columns exhibited only a small increase in bleeding rate at 370°C. The Rtx-200 column (not included in Fig. 3) was only used up to 350°C with a bleeding rate comparable to that of the XTI-5 column.
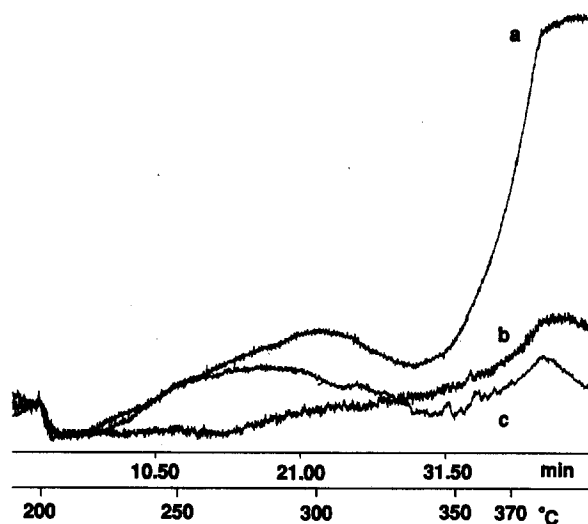

Fig. 3. Bleeding rates from (a) the CP-Sil 8 column, (b) the silabiphenyl column and (c) the XTI-5 column. Temperature programming as in Fig. 2.

Retention indices

If retention indices are calculated according to Kováts [33], using n-alkanes as standard compounds, dramatic changes in retention indices between columns of different polarities can be observed. Changes in retention indices with temperature have also often been reported (e.g., [34]). In this work where the solutes and standards are of the same types, such differences should be very small. In order to confirm this assumption, different programming rates (5 or 7°C/min) and different column head pressures (0.5 or 0.7 atm) were employed on the Rtx-200 column. With a test mixture composed of lower-molecular-weight PAHs, the retention index dependence on these parameters could be studied. For example, benzo[a]pyrene showed a retention index of 455.70 when the head pressure was held at 0.5 atm at a programming rate of 7°C/min. The elution temperature was 237°C. On the other hand, with a head pressure of 0.7 atm and a programming rate of 5°C min, the elution temperature of benzo[a]pyrene was 218°C and the corresponding retention index was 455.20. The same column was further evaluated in a different chromatograph (HP 5790) with helium as carrier gas. This change of chromatograph did not have a significant influence the retention indices of the PAHs. However, a more polarizable column could be expected to be more sensitive to temperature changes. Surprisingly, the retention index for benzo[c]picene on the silabiphenyl column, determined with the coronene–benzo[a]coronene system, was 145.68 for an elution temperature of 308°C and 145.10 at 319°C. Hence changes in elution temperature of up to 20°C have small effects on the retention indices for the two PAH systems evaluated.

Finally, retention indices for the standard mixture consisting of lower molecular weight PAHs were determined for the four columns and compared with the values reported in ref. 31. The results from these tests are given in Table II, where the precision (standard deviation) is also presented. All the columns showed higher retention index values for the solutes than the values in ref. 31. The differences were smallest for the CP-Sil 8 column. This was as expected, because the retention indices in ref. 31 were obtained on an SE-52 column (having 5% phenyl substitution). Both the non-polar and the most polar columns showed substantially different

TABLE II

TEMPERATURE-PROGRAMMED AVERAGE RETENTION INDICES (I) OF SOME LOWER-MOLECULAR-WEIGHT PAHs ON THE FOUR DIFFERENT COLUMNS

Compound	$I \pm$ S.D.				
	Rtx-200	CP-Sil 8	XTI-5	Silabiphenyl	Ref. 31
Pyrene	352.46 ± 0.14^b	351.47 ± 0.07^a	351.88 ± 0.04^c	352.19 ± 0.04^a	351.22 ± 0.08^c
Benzo[e]pyrene	454.22 ± 0.14^b	452.14 ± 0.09^a	452.71 ± 0.05^c	454.33 ± 0.09^a	450.73 ± 0.17^b
Benzo[a]pyrene	455.61 ± 0.18^b	453.74 ± 0.09^a	454.38 ± 0.05^c	455.72 ± 0.09^a	$453.44 \pm -^a$

[a] Two determinations.
[b] Three determinations.
[c] Four determinations.

values. The retention indices for benzo[e]pyrene on these columns were 3.5 and 3.6 index units (i.u.) higher than on the SE-52 column [31].

In Tables III and IV are given the retention indices of PAHs with MW 328 in the picene and coro-

nene standard system, respectively. The precision is better with the coronene standard. Further, the precision is lower for the higher-molecular-weight PAHs than for the smaller PAHs listed in Table II. However, the calculated standard deviations in Ta-

TABLE III

TEMPERATURE-PROGRAMMED AVERAGE RETENTION INDICES OF SOME PAHs MEASURED WITH THE PICENE STANDARD SERIES COMPOUNDS

The numbers refer to compounds in Fig. 1.

Compound	$I \pm$ S.D.			
	Rtx-200	CP-Sil 8	XTI-5	Silabiphenyl
Picene	500	500	500	500
1	492.60	509.79	509.74	502.45
Coronene	551.67 ± 0.70^a	548.36 ± 0.25^b	549.10 ± 0.59^a	553.94 ± 0.39^b
2	552.65	567.47	566.87	563.05
3	570.10	567.36	575.96	572.16
4	590.92	588.45	588.03	585.61
5	593.70	591.00	590.43	587.47
6	596.12	594.13	593.04	591.90
7	597.47	596.20	595.80	594.50
8	598.44	597.49	597.51	596.24
9	600	599.06	599.03	597.88
Benzo[c]picene	600	600	600	600
10	607.31	605.73	605.47	611.03
11	617.81	615.51	615.18	620.51
12	625.31	620.00	618.78	626.24
13	628.67	622.78	622.70	630.25
14	629.34	624.28	624.03	631.54
Benzo[a]coronene	659.18 ± 1.52^c	655.84 ± 0.23^b	656.34 ± 1.09^a	663.24 ± 0.56^b
Dinaphtho[2,1-a:2,1-h]anthrancene	700	700	700	700

[a] Twenty determinations.
[b] Ten determinations.
[c] Seventeen determinations.

TABLE IV

TEMPERATURE-PROGRAMMED AVERAGE RETENTION INDICES OF SOME PAHs MEASURED WITH THE CORO-NENE STANDARD SERIES COMPOUNDS

The numbers refer to compounds in Fig. 1.

Compound	$I \pm$ S.D.			
	Rtx-200	CP-Sil 8	XTI-5	Silabiphenyl
Picene[a]	49.33	52.49	51.45	46.42
1[a]	40.63	62.13	60.93	48.75
Coronene	100	100	100	100
2	100	118.67	117.63	109.18
3	118.03	127.45	126.52	118.04
4	138.33	139.50	138.48	132.67
5	141.19	141.83	140.81	133.31
6	143.46	144.93	143.89	137.67
7	144.46	147.15	146.32	140.18
8	145.44	148.32	147.55	141.63
9	146.47	149.90	149.19	143.61
Benzo[c]picene	147.38 ± 0.49[b]	150.69 ± 0.12[c]	150.31 ± 0.39[d]	145.68 ± 0.13[c]
10	154.08	155.72	155.11	155.15
11	163.19	164.36	163.70	163.29
12	170.53	168.37	167.47	168.12
13	172.70	170.87	170.25	171.58
14	173.48	172.12	171.53	172.77
Benzo[a]coronene	200	200	200	200
Dinaphtho[2,1-a:2,1-h]antracene[a]	235.70	239.07	238.27	231.63

[a] Extrapolated values from coronene–benzo[a]coronene.
[b] Sixteen determinations.
[c] Ten determinations.
[d] Twenty determinations.

ble II are based on a smaller number of observations.

The results obtained on the CP-Sil 8 and XTI-5 columns are similar, which is reasonable according to the results for the smaller PAHs. The ΔI values (measured as I on one column minus I on the CP-Sil 8 column) for the compounds in Tables III and IV are listed in Tables V and VI, respectively. By comparing the change in retention index of the reference compounds in the two standard systems, it can be concluded that the Rtx-200 column (the least polar) follows the same trend as the CP-Sil 8 column. The differences in retention indices for coronene and benzo[a]coronene in the picene standard system (Table V) are 3.31 and 3.34 i.u. higher than those on the CP-Sil 8 column. This implies that both coronene and benzo[a]coronene are influenced to the same extent. The ΔI values for the XTI-5 column are smaller, but also different for the standard com-

pounds, i.e., a difference of 0.74 and 0.50 i.u. for coronene and benzo[a]coronene, implying different retention mechanisms acting on the solutes at different temperatures. The column coated with the most polarizable stationary phase, silabiphenyl, shows different ΔI values for coronene and benzo[a]coronene, which were 5.58 and 7.40 i.u. higher than those on CP-Sil 8, respectively. From this it can be concluded that the forces that influence the solute retention are different at different temperatures also on this column.

Among the compounds studied, a few showed great differences in retention indices between columns. Most significant were the values for compound 1 (Fig. 1), which eluted prior to picene on the Rtx-200 column (Table III). This solute is non-planar and thereby probably more sensitive to the stationary phase composition. Further, compounds 2, also non-planar, and 3 show large differences in re-

TABLE V

ΔI-VALUES IN THE PICENE STANDARD SERIES COMPARED WITH CP-Sil 8

The number refer to compounds in Fig. 1.

Compound	ΔI			
	Rtx-200	XTI-5	Silabiphenyl	
Picene	0	0	0	
1	−17.19	−0.05	−7.34	
Coronene	3.31	0.74	5.58	
2	−14.82	−0.60	−4.42	
3	−6.26	−0.40	−4.20	
4	2.47	−0.42	−2.84	
5	2.70	−0.57	−3.53	
6	1.99	−1.09	−2.23	
7	1.27	−0.40	−1.70	
8	0.95	0.02	−1.25	
9	0.94	−0.03	−1.18	
Benzo[c]picene	0	0	0	
10	1.58	−0.26	5.30	
11	2.08	−0.33	5.00	
12	5.31	−1.22	6.24	
13	5.89	−0.08	7.47	
14	5.06	−0.25	7.26	
Benzo[a]coronene	3.34	0.50	7.40	
Dinaphtho[2,1-a:2,1-h]anthracene	0	0	0	

TABLE VI

ΔI-VALUES IN THE CORONENE STANDARD SERIES COMPARED TO CP-Sil 8

The number refer to compounds in Fig. 1.

Compound	ΔI			
	Rtx-200	XTI-5	Silabiphenyl	
Picene	−3.16	−1.04	−6.07	
1	−21.5	−1.20	−13.38	
Coronene	0	0	0	
2	−18.67	−1.04	−9.49	
3	−9.42	−0.93	−9.41	
4	−1.17	−1.02	−6.83	
5	−0.64	−1.02	−6.19	
6	−1.47	−1.04	−7.26	
7	−2.69	−0.83	−6.97	
8	−2.88	−0.77	−6.69	
9	−3.43	−0.71	−6.29	
Benzo[c]picene	−3.31	−0.38	−5.01	
10	−1.64	−0.61	−0.57	
11	−1.17	−0.66	−1.24	
12	2.16	−0.90	−0.25	
13	1.83	−0.62	0.71	
14	1.36	−0.59	0.65	
Benzo[a]corone	0	0	0	
Dinaphtho[2,1-a:2,1-h]anthracene	−3.37	−0.80	−7.44	

tention index between columns. Owing to their non-planar properties, compounds **1** and **2** have been used in LC for the evaluation of the retention characteristics of stationary phases [35]. Decreased retention was attributed to structural difficulties with fitting the compound geometrically in the stationary phase.

Applications

As an application of the utility of these columns (the Rtx-200 column was not included), a previously separated HPLC fraction of an SRM 1597 sample containing PAHs with MW 328 was chromatographed. The injection mode and temperature programme were the same as described for the high-
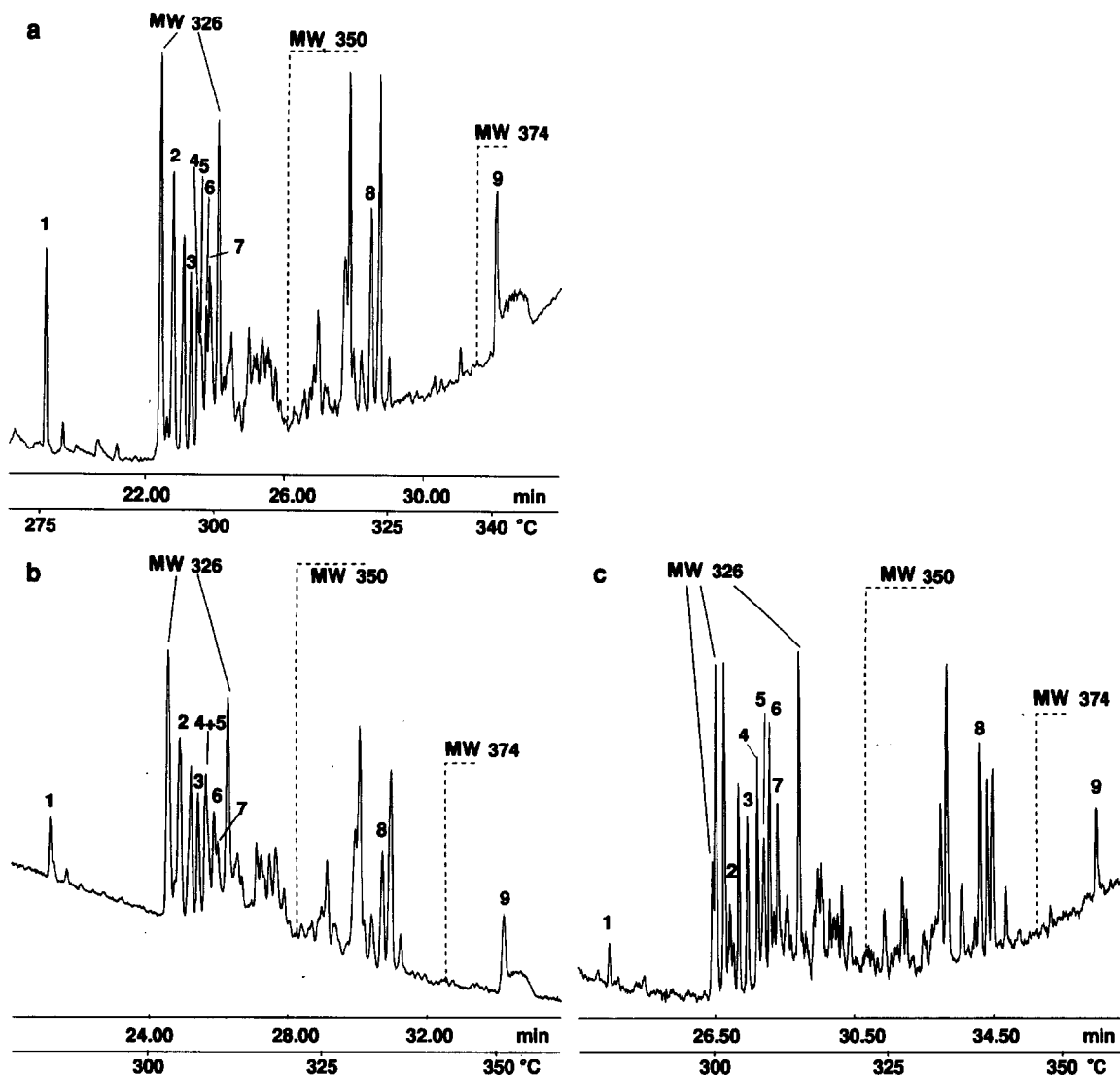
Fig. 4. Gas chromatograms (flame ionization detection) of SRM 1597 sample, previously fractionated by HPLC, injected together with the two standard series compounds on (a) the CP-Sil 8 column, (b) the XTI-5 column and (c) the silabiphenyl column. Temperature programming as in Fig. 2. Peaks: 1 = coronene; 2 = **4**; 3 = **6**; 4 = **7**; 5 = **8**; 6 = **9**; 7 = benzo[c]picene; 8 = benzo[a]coronene; 9 = dinaphtho[2,1-a:2,1-h]anthrancene. The bold numbers refer to the compounds in Fig. 1.

molecular-weight PAHs under Experimental. After GC with flame ionization detection, the columns were mounted in a Finnigan MAT Incos 50 mass spectrometer and run in the electron impact mode at 70 eV with a transfer line temperature of 350°C. The molecular weights were determined by means of the molecular ions. As is demonstrated in Fig. 4, this sample contained not only PAHs with MW 328 but also at least three with MW 326 and at least nine compounds with MW 350. Traces of the ions having m/z 340, 352 and 354 could also be observed. The mass spectra indicated seven isomers having MW 328. Thus, in Fig. 4c, eight peaks of MW 328 were found, of which one was the standard compound benzo[c]picene, peak 7 in Fig. 4. By comparing peak resolution it can be seen that the silabiphenyl column has the possibility of resolving more peaks than the CP-Sil 8 and XTI-5 columns for this sample.

The retention indices were calculated and compared with those in Tables III and IV. Five possible isomers having MW 328 were suggested. These are numbered and listed in the caption of Fig. 4.

CONCLUSIONS

High-temperature GC offers the possibility of analysing a variety of PAHs with molecular weights up to at least 400. There are a number of capillary columns available that are suitable for the task, although we have shown that further developments can give columns with better compatibility/solubility and efficiency for high-molecular-weight PAHs. Use of the retention index systems presented in this paper together with mass spectral data offers a good possibility of identifying and determining PAHs in the mass range discussed. The method is a preferred alternative to ordinary HPLC owing to its higher chromatographic efficiency and to micro-LC from the viewpoint of analysis time. Further, the different retention properties for columns with different stationary phase compositions can make GC suitable for studies of compound-specific properties such as polarizability.

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