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Retention Behaviour of Alkylated and Non-Alkylated Polycyclic Aromatic Hydrocarbons on Different Types of Stationary Phases in Gas Chromatography

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Abstract: The gas chromatographic retention behaviour of 16 polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs on a new ionic liquid stationary phase, 1,12-di(tripropylphosphonium) dodecane bis(trifluoromethanesulfonyl)imide (SLB®-ILPAH) intended for the separation of PAH mixtures, was compared with the elution pattern on more traditional stationary phases: a non-polar phenyl arylene (DB-5ms) and a semi-polar 50% phenyl dimethyl siloxane (SLB PAHms) column. All columns were tested by injections of working solutions containing 20 parental PAHs from molecular weight of 128 to 278 g/mol and 48 alkylated PAHs from molecular weight of 142 to 280 g/mol on a one dimensional gas chromatography-mass spectrometry (GC-MS) system. The SLB PAHms column allowed separation of most isomers. The SLB®-ILPAH column showed a rather different retention pattern compared to the other two columns and, therefore, provided a potential for use in comprehensive two-dimensional GC (GC×GC). The ionic liquid column and the 50% phenyl column showed good thermal stability with a low bleed profile, even lower than that of the phenyl arylene "low bleed" column.

Keywords: ionic liquid stationary phase; gas chromatography; chromatographic selectivity; alkylated polycyclic aromatic hydrocarbons (alkylated PAHs)

1. Introduction

Ubiquitously present in the environment, polycyclic aromatic hydrocarbons (PAHs) originate from natural and anthropogenic incomplete combustion processes. They are present in air, food, water and soil. Nowadays, the PAHs originating from anthropogenic activities are unarguably predominant compared to those originating from natural sources. Humans are exposed to PAHs in almost every aspect of everyday life and, therefore, PAHs are among the most studied chemicals. During the last 50 years, the procedures for the determination of individual PAHs in complex environmental mixtures have been extensively developed and improved. In 1976, 16 specific PAHs were selected for regulation by the United States Environmental Protection Agency (U.S. EPA); the historical perspectives regarding the choice of these 16 EPA PAHs can be found in an article by Keith [1].

In 2002, the toxicities of 33 PAHs were assessed by The European Scientific Committee on Food and 15 PAHs showed clear evidence of mutagenicity/genotoxicity. Fourteen of these 15 PAHs showed clear carcinogenic effects in various types of bioassays and in experimental animals [2]. Seven of these carcinogenic PAHs in the Scientific Committee on Food study are also contained in the EPA's set of 16 PAHs, while the additional seven are: benzo(*j*)fluoranthene, cyclopenta(*cd*)pyrene, dibenzo(*a*,*e*)-, dibenzo(*a*,*h*)-, dibenzo(*a*,*i*)-, dibenzo(*a*,*l*)pyrene and 5-methylchrysene. In 2006, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) concluded that benzo(*c*)fluorene is probably also carcinogenic [3]. This shows that the list of the toxic and environmentally relevant PAHs is still growing.

In non-occupational settings, food is the main source of human exposure to PAHs, followed by cigarette smoke, which in some cases may result in PAH exposure on par with the food uptake route [4,5]. Other important exposure routes include traffic related air pollution and all kinds of occupational exposures. Nonetheless, the new possible exposure pathways are still being identified: e.g. synthetic turf materials used on football fields [6].

The analysis of PAHs is generally based on gas chromatography (GC) rather than on liquid chromatography (LC) because GC allows greater selectivity, resolution and sensitivity than LC [7,8]. The GC systems are commonly coupled with flame ionisation detectors (FID) or mass-spectrometric detectors (MS). The GC analysis was conventionally based on non-polar stationary phases operated at relatively high temperatures [8,9]. The 5% phenyl methylpolysiloxane phase (like in the DB-5 column) is still the most often applied one in PAHs analysis and it has also been recommended in a number of US-EPA methods, e.g. US EPA method 610 [10]. Since the 1990s, high phenyl content stationary phases have been more frequently used, e.g. described by the producers as "50% phenyl methylpolysiloxane-like" DB-17MS [8,11], Rxi-PAH [12] or SLB PAHms [13].

Some years ago, a new group of stationary phases, based on non-bonded ionic liquids (IL) was introduced [14,15]. Based on non-molecular solvents with low melting points, these stationary phases consist of organic cations plus inorganic or organic anions [16] and, therefore, the IL columns enable chromatographic separation based on a selectivity different to that provided by conventional stationary phases. Some IL columns can exhibit "dual nature" features; they allow separation of non-polar molecules as non-polar stationary phases do, while at the same time they have a high affinity for polar molecules like polyethylene glycol (wax) and cyanopropyl-siloxane stationary phases. The IL columns are more polar than the wax columns but they have higher thermal stability compared to traditional siloxane phases with a similar selectivity because they are not susceptible to back-biting reactions that result in phase degradation and column bleed [14]. Siloxane-based stationary phases contain active hydroxyl groups at the terminal positions; this makes them sensitive to the oxygen catalyzed cleavage of backbone siloxane. The siloxane chain then breaks to volatile cyclic siloxanes that elute from the column as "bleed" and results in a rising baseline.

So far, the chromatographic properties of the IL columns have only been investigated in a few studies. The IL columns have been used for the separation of different classes of environmental pollutants, like polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and other chlorinated compounds [17,18], alkyl phosphates, fatty acids, and petroleum distillates [19]. A new IL column, SLB®-ILPAH, intended for the separation of PAHs mixtures, recently became commercially available. This column has already been tested in terms of the retention behaviour of alkyl-substituted polycyclic aromatic sulphur heterocyclic isomers [13].

In this study, we investigated the retention behaviour of PAHs and alkylated PAHs on the SLB®-ILPAH column and two stationary phases traditionally used for the PAH analysis: a low bleed column with a phenyl arylene polymer that is virtually equivalent to a (5%-phenyl)-methylpolysiloxane (DB-5ms) and a high phenyl content column denoted as 50% phenyl-dimethylpolysiloxane (SLB PAHms). The difference between the arylene column and a 5% phenyl-dimethylsiloxane column is that in the arylene column, the phenyl ring is built in the siloxane chain, whereas in the phenyl-dimethylsiloxane phase, the phenyl rings are positioned as substituents (side chains). Alkylated PAHs were selected because numerous isomers of these compounds are currently targeted in analyses of environmental samples.

Alkylated PAHs are recognised as environmental pollutants although they are still not regularly included in the analysis of priority PACs (e.g. 16 EPA PAHs). They are ubiquitously present in the environment and are often more toxic than the parental PAHs [20,21]. Alkylated PAHs have been found in the toxic fractions in several Effect Directed Analysis (EDA) studies [22–25]. 5-methylchrysene, 1-methylpyrene and 7,12-dimethylbenz(*a*)anthracene, as confirmed toxic compounds, are being included more and more in standard PAH analyses [26,27]. A list of 34 PAHs (18 parental PAHs and 16 alkylated), has been recommended for toxicological screenings by the US EPA [28]. In addition

to the 16 traditional EPA PAHs, the list of 34 PAHs includes perylene, benzo(*e*)pyrene and 16 groups of C-1 to C-4 alkyl derivatives.

The determination of alkylated PAHs in complex environmental samples is problematic because of numerous coeluting isomers [19,29]. It is not possible to separate all isomers of heavier PAHs in a single chromatographic run on one column but two-dimensional GC-MS analysis (GC×GC-MS) could offer a solution. GC×GC can only be fruitful if the two columns used in series are (semi-) orthogonal, or, as chemically different from each other as possible. Therefore, an assessment of new and different stationary phases with different separation mechanisms was needed.

This study investigates the retention behaviour of 20 parental PAHs from molecular weight (MW) 128 to 278 g/mol and 48 alkylated PAHs on three stationary phases. The isomeric sets of alkyl PAHs investigated here are: methyl- and dimethyl-naphthalenes (128-C1, 128-C2), methyl-phenanthrenes and anthracenes (178-C1), methyl-fluoranthene and pyrene (202-C1), methyl- and dimethyl- benz(*a*)anthracenes, benzo(*c*)phenanthrenes and chrysenes (228-C1, 228-C2) and methyl benzo(*a*)pyrenes (252-C1).

2. Materials and Methods

Table 1 shows the characteristics of the three stationary phases that were tested in this study. The columns SLB PAHms and SLB®-ILPAH (both from Supelco, Bellefonte, Pennsylvania, USA) were made available by Sigma Aldrich (Zwijndrecht, The Netherlands) and the DB-5ms was bought from Agilent, The Netherlands. The parental and alkylated-PAHs standard solutions and pure compounds (Table 2) were purchased from Sigma Aldrich (Zwijndrecht, The Netherlands). All solvents used (isooctane and toluene) were obtained in picograde quality from Merck Millipore (Amsterdam, The Netherlands).

Table 1. Stationary phases and their characteristics.

GC Column	Stationary Phase	Dimensions	Max. temp. (Isotherm/ Programmed) °C
VDB-5ms	Phenyl Arylene polymer, virtually equivalent to 5%-phenyl-methylpolysiloxane	30 m × 0.25 mm ID × 0.25 µm	300/320 °C
SLB PAHms (Supelco)	Denoted as 50% phenyl dimethylpolysiloxane	30 m × 0.25 mm ID × 0.25 µm	350/360 °C
SLB®-ILPAH (Supelco)	Non-bonded, 1,12-Di(tripropylphosphonium) dodecane bis(trifluoromethanesulfonyl)imide	20 m × 0.18 mm ID × 0.05 µm	300/300 °C

All standards were gravimetrically prepared in toluene and isooctane. The working solutions were prepared by mixing appropriate volumes from the individual stock solutions. Analyses were performed on an Agilent 6890 gas chromatograph coupled to an Agilent 5975C inert MSD with a Triple-Axis Detector. All injections were performed in the splitless mode (1 µL; splitless time 1.4 min) at 275 °C and with MS operating in total ion current mode. The oven temperature programs were set as follows: DB-5ms and SLB-PAH: isothermal at 90 °C for 10 min, then with 5 °C/min to 300 °C, SLB®-ILPAH: isothermal at 90 °C for 6 min, then with 5 °C/min to 300 °C.

The temperature programs were optimised in order to compare the elution order and peak resolution between the columns.

The SLB®-ILPAH is commercially available in dimensions different from the "standard" dimensions (Table 1) as discussed in the Results and discussion section.

Table 2. PAHs and alkylated PAHs: retention times (RT) and relative retention times (RRT) in minutes. RRTs were calculated relative to pyrene. The coeluting isomers are marked: green (overlap > 90%), blue (90% < overlap > 50%) and orange (overlap < 50%).

Code	DB-5ms	RT	RRT	Code	SLB PAHms	RT	RRT	Code	SLB-ILPAH	RT	RRT
N	Naphthalene	13.20	0.353	N	Naphthalene	16.12	0.379	N	Naphthalene	5.86	0.188
N2	2-Methylnaphthalene	17.65	0.472	N2	2-Methylnaphthalene	20.03	0.471	N2	2-Methylnaphthalene	9.13	0.292
N1	1-Methylnaphthalene	18.19	0.486	N1	1-Methylnaphthalene	20.82	0.489	N1	1-Methylnaphthalene	9.33	0.299
N2,6	2,6-Dimethylnaphthalene	21.25	0.568	N2,6	2,6-Dimethylnaphthalene	23.31	0.548	N2,7	2,7-Dimethylnaphthalene	12.07	0.386
N2,7	2,7-Dimethylnaphthalene	21.31	0.570	N2,7	2,7-Dimethylnaphthalene	23.35	0.549	N2,6	2,6-Dimethylnaphthalene	12.11	0.388
N1,3	1,3-Dimethylnaphthalene	21.66	0.579	N1,3	1,3-Dimethylnaphthalene	24.04	0.565	N1,3	1,3-Dimethylnaphthalene	12.14	0.389
N1,6	1,6-Dimethylnaphthalene	21.78	0.583	N1,6	1,6-Dimethylnaphthalene	24.05	0.565	N1,6	1,6-Dimethylnaphthalene	12.21	0.391
N1,4	1,4-Dimethylnaphthalene	22.22	0.594	N1,4	1,4-Dimethylnaphthalene	24.73	0.581	N1,4	1,4-Dimethylnaphthalene	12.21	0.391
N1,5	1,5-Dimethylnaphthalene	22.31	0.597	N1,5	1,5-Dimethylnaphthalene	24.87	0.584	N1,5	1,5-Dimethylnaphthalene	12.34	0.395
Al	Acenaphthylene	22.53	0.603	N1,2	1,2-Dimethylnaphthalene	25.26	0.593	N1,2	1,2-Dimethylnaphthalene	13.23	0.424
N1,2	1,2-Dimethylnaphthalene	22.65	0.606	Al	Acenaphthylene	25.96	0.610	N1,8	1,8-Dimethylnaphthalene	13.72	0.439
N1,8	1,8-Dimethylnaphthalene	23.25	0.622	N1,8	1,8-Dimethylnaphthalene	26.17	0.615	At	Acenaphthene	13.72	0.439
At	Acenaphthene	23.48	0.628	At	Acenaphthene	26.66	0.626	N1,6,7	1,6,7-Trimethylnaphthalane	15.83	0.507
N1,6,7	1,6,7-Trimethylnaphthalane	25.59	0.684	N1,6,7	1,6,7-Trimethylnaphthalane	27.82	0.654	Al	Acenaphthylene	15.88	0.508
Fl	Fluorene	26.13	0.699	Fl	Fluorene	29.38	0.690	Fl	Fluorene	17.29	0.554
Ph	Phenanthrene	30.75	0.822	Ph	Phenanthrene	34.88	0.819	Ph	Phenanthrene	23.84	0.763
A	Anthracene	30.99	0.829	A	Anthracene	35.10	0.825	A	Anthracene	23.98	0.768
Ph2	2-Methylphenanthrene	33.25	0.889	Ph2	2-Methylphenanthrene	37.22	0.874	45MP	4,5-Methylenephenanthrene	25.49	0.816
An2	2-Methylanthracene	33.47	0.895	An2	2-Methylanthracene	37.38	0.878	Ph2	2-Methylphenanthrene	25.89	0.829
45MP	4,5-Methylenephenanthrene	33.55	0.897	An1	1-Methylanthracene	37.64	0.884	An1	1-Methylanthracene	25.93	0.830
An1	1-Methylanthracene	33.68	0.901	Ph1	1-Methylphenanthrene	37.90	0.890	An2	2-Methylanthracene	26.03	0.833
Ph1	1-Methylphenanthrene	33.73	0.902	45MP	4,5-Methylenephenanthrene	37.92	0.891	Ph1	1-Methylphenanthrene	26.15	0.837
An9	9-Methylanthracene	34.40	0.920	An9	9-Methylanthracene	38.84	0.912	An9	9-Methylanthracene	26.58	0.851
Ph3,6	3,6-Dimethylphenanthrene	35.36	0.946	Ph3,6	3,6-Dimethylphenanthrene	38.87	0.913	Ph3,6	3,6-Dimethylphenanthrene	27.72	0.888
Fa	Fluoranthene	36.39	0.973	An2,3	2,3-Dimethylanthracene	40.64	0.955	Ph9,10	9,10-Dimethylanthracene	28.90	0.925
An2,3	2,3-Dimethylanthracene	36.63	0.980	Fa	Fluoranthene	41.16	0.967	An2,3	2,3-Dimethylanthracene	29.10	0.932
Py	Pyrene	37.39	1.000	An9,10	9,10-Dimethylanthracene	42.36	0.995	Fa	Fluoranthene	30.42	0.974
An9,10	9,10-Dimethylanthracene	37.63	1.006	Py	Pyrene	42.57	1.000	Py	Pyrene	31.23	1.000
Fa2	2-Methylfluoranthene	38.58	1.032	Fa2	2-Methylfluoranthene	43.11	1.013	Fl2	2-Methylfluoranthene	32.29	1.034
Py1	1-Methylpyrene	40.07	1.072	Py1	1-Methylpyrene	45.25	1.063	Bc1	1-Methylbenzo(*c*)phenanthrene	33.37	1.069
Bc1	1-Methylbenzo(*c*)phenanthrene	42.36	1.133	Bc1	1-Methylbenzo(*c*)phenanthrene	47.71	1.121	Py1	1-Methylpyrene	33.43	1.070
Ba	Benz(*a*)anthracene	43.12	1.153	Bc2	2-Methylbenzo(*c*)phenanthrene	48.63	1.142	Bc2	2-Methylbenzo(*c*)phenanthrene	35.98	1.152
T	Triphenylene	43.22	1.156	Ba	Benz(*a*)anthracene	48.68	1.144	Bc1,12	1,12-Dimethylbenzo(*c*)phenanthrene	36.46	1.168
C	Chrysene	43.27	1.157	T	Triphenylene	49.00	1.151	Bc4	4-Methylbenzo(*c*)phenanthrene	36.72	1.176
Bc2	2-Methylbenzo(*c*)phenanthrene	43.49	1.163	C	Chrysene	49.07	1.153	Bc3	3-Methylbenzo(*c*)phenanthrene	36.77	1.178
23BA	2,3-Benzanthracene	43.72	1.169	Bc3	3-Methylbenzo(*c*)phenanthrene	49.42	1.161	Bc5	5-Methylbenzo(*c*)phenanthrene	36.82	1.179
Bc3	3-Methylbenzo(*c*)phenanthrene	44.11	1.180	23BA	2,3-Benzanthracene	49.51	1.163	Ba	Benz(*a*)anthracene	37.29	1.194

Table 2. *Cont.*

Code	DB-5ms	RT	RRT	Code	SLB PAHms	RT	RRT	Code	SLB-ILPAH	RT	RRT
Bc5	5-Methylbenzo(*c*)phenanthrene	44.39	1.187	Bc5	5-Methylbenzo(*c*)phenanthrene	49.90	1.172	C	Chrysene	37.43	1.199
Bc4	4-Methylbenzo(*c*)phenanthrene	44.45	1.189	Bc4	4-Methylbenzo(*c*)phenanthrene	49.98	1.174	T	Triphenylene	37.56	1.203
Ba2	2-Methylbenz(*a*)anthracene	44.92	1.201	Ba2	2-Methylbenz(*a*)anthracene	50.13	1.178	23Ba	2,3-Benzanthracene	37.85	1.212
Ba1	1-Methylbenz(*a*)anthracene	44.92	1.201	Ba7	7-Methylbenz(*a*)anthracene	50.39	1.184	Ba1	1-Methylbenz(*a*)anthracene	37.85	1.212
Ba7	7-Methylbenz(*a*)anthracene	45.08	1.206	Ba9	9-Methylbenz(*a*)anthracene	50.47	1.186	C5	5-Methylchrysene	38.41	1.230
Ba9	9-Methylbenz(*a*)anthracene	45.08	1.206	Ba1	1-Methylbenz(*a*)anthracene	50.52	1.187	C4	4-Methylchrysene	38.51	1.234
Ba6	6-Methylbenz(*a*)anthracene	45.16	1.208	Ba6	4-Methylbenz(*a*)anthracene	50.52	1.187	Ba6	6-Methylbenz(*a*)anthracene	38.70	1.240
Ba4	4-Methylbenz(*a*)anthracene	45.16	1.208	Ba4	6-Methylbenz(*a*)anthracene	50.52	1.187	Ba4	4-Methylbenz(*a*)anthracene	38.70	1.240
C5	5-Methylchrysene	45.33	1.212	Ba3	3-Methylbenz(*a*)anthracene	50.96	1.197	Ba2	2-Methylbenz(*a*)anthracene	38.76	1.242
C6	6-Methylchrysene	45.42	1.215	Ba5	5-Methylbenz(*a*)anthracene	50.96	1.197	Ba9	9-Methylbenz(*a*)anthracene	38.85	1.244
Ba3	3-Methylbenz(*a*)anthracene	45.42	1.215	C6	6-Methylchrysene	51.03	1.199	Ba7	7-Methylbenz(*a*)anthracene	38.91	1.246
C4	4-Methylchrysene	45.42	1.215	C5	5-Methylchrysene	51.12	1.201	C6	6-Methylchrysene	39.13	1.253
Ba5	5-Methylbenz(*a*)anthracene	45.42	1.215	C4	4-Methylchrysene	51.25	1.204	Ba3	3-Methylbenz(*a*)anthracene	39.13	1.253
Bc1,12	1,12-Dimethylbenzo(*c*)phenanthrene	45.49	1.217	Ba6,8	6,8-Dimethylbenz(*a*)anthracene	51.26	1.204	Ba5	5-Methylbenz(*a*)anthracene	39.13	1.253
Ba10	10-Methylbenz(*a*)anthracene	45.95	1.229	Ba10	10-Methylbenz(*a*)anthracene	51.73	1.215	Ba10	10-Methylbenz(*a*)anthracene	39.45	1.264
Ba6,8	6,8-Dimethylbenz(*a*)anthracene	46.74	1.250	Bc1,12	1,12-Dimethylbenzo(*c*)phenanthrene	51.91	1.219	Ba6,8	6,8-Dimethylbenz(*a*)anthracene	39.61	1.269
Ba3,9	3,9-Dimethylbenz(*a*)anthracene	46.93	1.255	Ba3,9	3,9-Dimethylbenz(*a*)anthracene	52.17	1.226	Ba7,12	7,12-Dimethylbenz(*a*)anthracene	39.71	1.272
BbF	Benzo(*b*)fluoranthene	47.82	1.279	Ba7,12	7,12-Dimethylbenz(*a*)anthracene	53.98	1.268	Ba3,9	3,9-Dimethylbenz(*a*)anthracene	40.37	1.293
Ba7,12	7,12-Dimethylbenz(*a*)anthracene	47.88	1.281	BbF	Benzo(*b*)fluoranthene	54.02	1.269	Ba8,9,11	8,9,11-Trimethylbenz(*a*)anthracene	41.40	1.326
BkF	Benzo(*k*)fluoranthene	47.94	1.282	BkF	Benzo(*k*)fluoranthene	54.12	1.271	BbF	Benzo(*b*)fluoranthene	42.86	1.373
BeP	Benzo(*e*)pyrene	48.88	1.307	Ba8,9,11	8,9,11-Trimethylbenz(*a*)anthracene	54.30	1.276	BkF	Benzo(*k*)fluoranthene	43.02	1.378
Ba8,9,11	8,9,11-Trimethylbenz(*a*)anthracene	49.03	1.311	BeP	Benzo(*e*)pyrene	55.61	1.306	BeP	Benzo(*e*)pyrene	44.04	1.411
BaP	Benzo(*a*)pyrene	49.08	1.313	BaP	Benzo(*a*)pyrene	55.86	1.312	BaP	Benzo(*a*)pyrene	44.08	1.412
BaP9	9-Methylbenzo(*a*)pyrene	50.71	1.356	BaP9	9-Methylbenzo(*a*)pyrene	57.19	1.343	BaP10	10-Methylbenzo(*a*)pyrene	45.24	1.449
BaP8	8-Methylbenzo(*a*)pyrene	50.84	1.360	BaP8	8-Methylbenzo(*a*)pyrene	57.39	1.348	BaP9	9-Methylbenzo(*a*)pyrene	45.49	1.457
BaP7	7-Methylbenzo(*a*)pyrene	51.07	1.366	BaP7	7-Methylbenzo(*a*)pyrene	57.71	1.356	BaP8	7-Methylbenzo(*a*)pyrene	45.49	1.457
BaP10	10-Methylbenzo(*a*)pyrene	51.12	1.367	BaP10	10-Methylbenzo(*a*)pyrene	57.94	1.361	BaP7	8-Methylbenzo(*a*)pyrene	45.49	1.457
BaP7,10	7,10-Dimethylbenzo(*a*)pyrene	52.93	1.416	BaP7,10	7,10-Dimethylbenzo(*a*)pyrene	59.77	1.404	BaP7,10	7,10-Dimethylbenzo(*a*)pyrene	46.27	1.482
	Indeno(1,2,3-*c*,*d*)pyrene	53.26	1.424		Indeno(1,2,3-*c*,*d*)pyrene	60.86	1.430		Dibenz(*a*,*h*)anthracene	48.68	1.559
	Dibenz(*a*,*h*)anthracene	53.44	1.429		Dibenz(*a*,*h*)anthracene	60.94	1.432		Indeno(1,2,3-*c*,*d*)pyrene	49.02	1.570
	Benzo(*g*,*h*,*i*)perylene	54.26	1.451		Benzo(*g*,*h*,*i*)perylene	62.89	1.477		Benzo(*g*,*h*,i)perylene	50.01	1.602

3. Results and discussion

The retention times and the relative retention times to pyrene of all parental PAHs and alkylated PAHs injected on the three columns are presented in Table 2. This table also shows the coelutions of the isomers having similar mass spectra (see coloured cells). The coelutions of PAHs that are not isomers (e.g. the coelution of 7,12-dimethylbenz(*a*)anthracene and benzo(*b*)fluoranthene or 2-methylbenzo(*c*)phenanthrene and benz(*a*)anthracene on the SLB PAHms column) were not marked here because these compounds have different mass spectra and can be separated by the MS detector. However, the interferences of the fragment ions of the overlapping compounds with different base peak ions must be taken into account for accurate quantitation.

The elution order of the PAHs and the alkyl-PAHs on the phenyl arylene and the 50% phenyl-polysiloxane stationary phases is rather similar. However, the elution order on the SLB-ILPAH is different; these differences will be discussed below. The advantages and shortcomings of the three studied columns are briefly summarized in Table 3.

Table 3. Chromatographic characteristics of the three columns: DB-5ms, SLB PAHms and SLB-ILPAH.

GC Columns	Phenyl Arylene	50% Phenyl Polysiloxane	SLB-ILPAH
Overlap > 90%	12 peaks	11 peaks	19 peaks
90% > overlap > 50%	7 peaks	2 peaks	3 peaks
Overlap < 50%	4 peaks	4 peaks	1 peak
Peak shape	Good	Good	Good
Analysis time	Long	Long	Shorter than on the other two columns
Bleeding	Substantial bleeding above 260 °C	No bleeding till 300 °C	No bleeding till 300 °C

The least polar column, phenyl arylene, shows an overlap of 19 isomers at more than 50% of the peak height and of 4 isomers at less than 50% of the peak height. Chrysene, one of the 16 EPA PAHs, coelutes with triphenylene but the rest of the 16 EPA PAHs are totally resolved. This column showed the best separation of dimethylnaphthalenes (Figure 1); 1,3- and 1,6-dimethylnaphthalenes were separated on this column only. Figure 1 shows that the dimethylnaphthalenes formed a co-eluting peaks' cluster on the ionic liquid column while on the siloxane-based columns they were much better separated. Figure 1 also shows that compared to the phenyl arylene column, the 50% phenyl-polysiloxane column shows a substantially better separation of the injected isomers. Table 2 shows that on this column only 13 isomers overlapped at more than 50% of the peak height and four isomers overlapped at less than 50% of the peak height.

Figure 2A shows that chrysene and triphenylene were partly separated on the 50% phenyl-polysiloxane column while they coeluted at the phenyl arylene column. The separation of these isomers is comparable to the separation achieved on the Rxi-PAH column (50% phenyl methylpolysiloxane-like phase) used for the PAHs analysis by Nalin et al. [12]. The study of Poster et al. [8] showed that chrysene and triphenylene coelute on the comparable DB-17MS stationary phase (50% phenyl methyl-polysiloxane-like phase), are partly resolved on the non-polar DB-XLB column (proprietary phase) and totally resolved on the LC-50 column (dimethyl/50% liquid crystalline phase). Figure 2A shows that chrysene and triphenylene are totally resolved on the IL column.

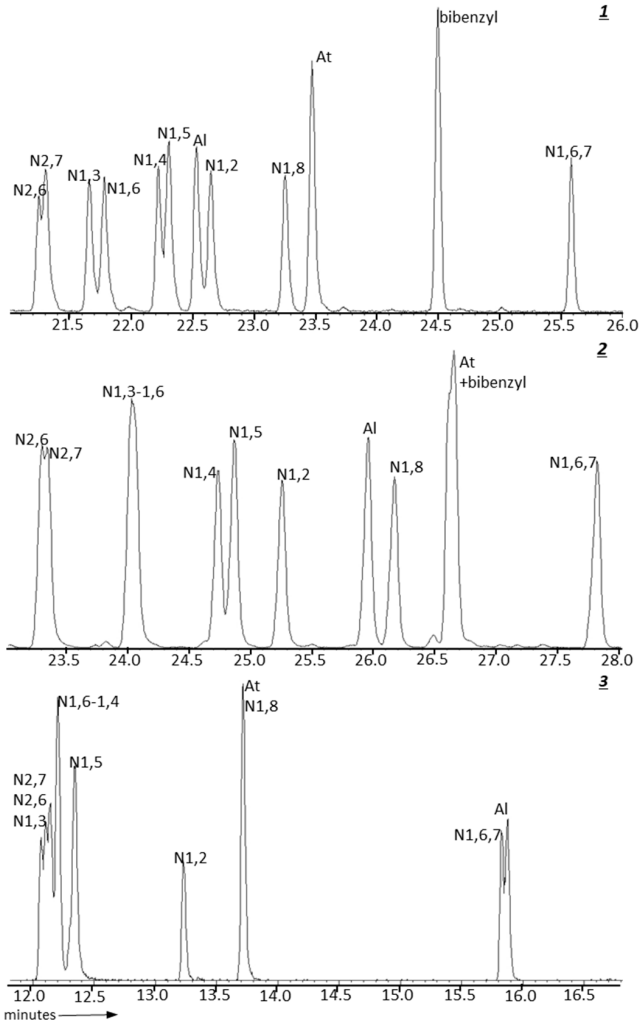

Figure 1. Elution order of dimethylnaphthalenes, trimethylnaphthalene, acenaphthylene (Al), acenaphthene (At) on phenyl arylene (**1**), 50% phenyl-polysiloxane (**2**) and SLB-ILPAH (**3**) stationary phases. For abbreviations see Table 2.

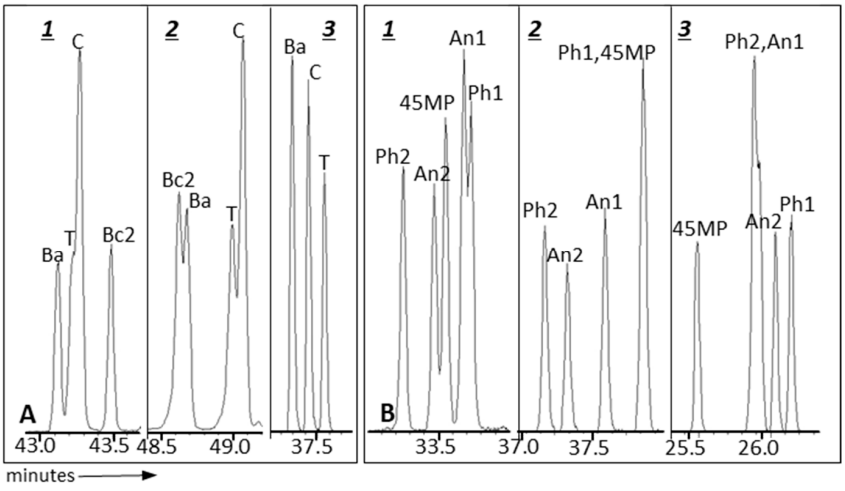

Figure 2. Elution order of 228-PAHs (**A**) and ethyl- anthracenes and phenanthrenes and 4,5-methylenephenanthrene (**B**) on phenyl arylene (**1**), 50% phenyl-polysiloxane (**2**) and SLB-ILPAH (**3**) stationary phases. For abbreviations see Table 2.

In Figure 2B we see that all isomers of methylated phenanthrenes and anthracenes were separated on the 50% phenyl-polysiloxane column, while some of these isomers coeluted on the phenyl arylene and on the SLB-ILPAH column. The IL column also demonstrated the different mechanism of retention; 4,5-methylenephenanthrene eluted before the methylated phenanthrenes and anthracenes (178-C1).

Figure 3 shows that the best separation of 17 methylated benz(*a*)anthracenes, benzo(*c*)phenanthrenes and chrysenes isomers (228-C1) was achieved on the 50% phenyl-polysiloxane column; only seven isomers coeluted at more than 90% of the peak height while the remaining 10 isomers were at least partly resolved (Table 2). This separation was better than the separation achieved on the phenyl arylene column, where 11 of these isomers coeluted, as well as on the SLB-ILPAH column, where 10 of these isomers coeluted. The number of the observed coelutions might be reduced by increasing the lengths of the tested columns, reducing the internal diameters and/or by improving the applied temperature programs with stable temperature periods around the elution times of isomeric clusters.

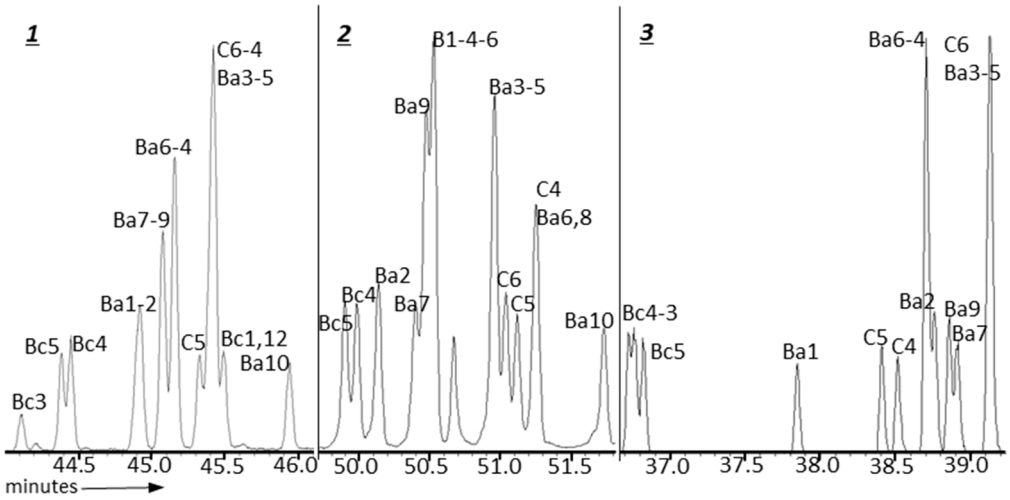

Figure 3. Elution order of methyl-benz(*a*)anthracenes, chrysenes and benzo(*c*)phenanthrenes and dimethylbenzo(*c*)phenanthrenes on phenyl arylene (**1**), 50% phenyl-polysiloxane (**2**) and SLB-ILPAH (**3**) stationary phases. For abbreviations see Table 2.

The commercially available SLB-ILPAH column was 2/3 the length of the two other columns. The internal diameter was 3/4 of that of the other two and the film thickness 1/5 of that of the two other columns, which made the separation substantially faster. However, it is not possible to compare the dimensions of the IL column to the siloxane-based columns directly because of the different nature of an IL coating resulting in the different type of interactions between the analytes and the stationary phase. This IL phase shows stronger retention for heavier PAHs (Table 2); the relative retention times of the heavier PAHs on this column are higher than on the phenyl arylene and the 50% phenyl-polysiloxane columns. The SLB-ILPAH phase also showed some interesting elution shifts: 1,12-dimethylbenzo(*c*)phenanthrene (228-C2) eluted before benz(*a*)anthracene and other PAHs with MWs of 228 g/mol and 1-methylbenzo(*c*)phenanthrene (228-C1) eluted before 1-methylpyrene (202-C1). Also, the elution order of four PAHs from the 16 EPA PAHs-group on this IL column is different compared to the elution on the two siloxane-based columns: acenaphthylene elutes before acenaphthene and dibenz(*a*,*h*)anthracene elutes before indeno(1,2,3-*cd*)perylene on the SLB-ILPAH column. However, the overall separation of the isomers on the SLB-ILPAH phase is not as good as on the other two phases: 22 isomers overlap at more than 50% of the peak height. A huge advantage of this column is the total separation of chrysene from triphenylene (Figure 2A). Yet, Figure 4 shows that the highly carcinogenic benzo(*a*)pyrene, another PAH belonging to the group of the 16 EPA PAHs, coeluted with benzo(*e*)pyrene. Both isomers are separated on the phenyl-siloxane column, while benzo(*a*)pyrene coelutes with 8,9,11-trimethylbenz(*a*)anthracene. Priority toxicant

5-methylchrysene was totally separated on this column while on the other two columns it could not be totally resolved from other isomers (Figure 3). The SLB-ILPAH column also managed to separate 1-methylbenz(*a*)anthracene and 4-methylchrysene; these isomers (partially) coelute on the other two columns. It is plausible that increasing the length of this column to 30 m may somewhat improve the observed coelutions, but it is unlikely the pattern would improve so much that it would equal that of the other two columns.

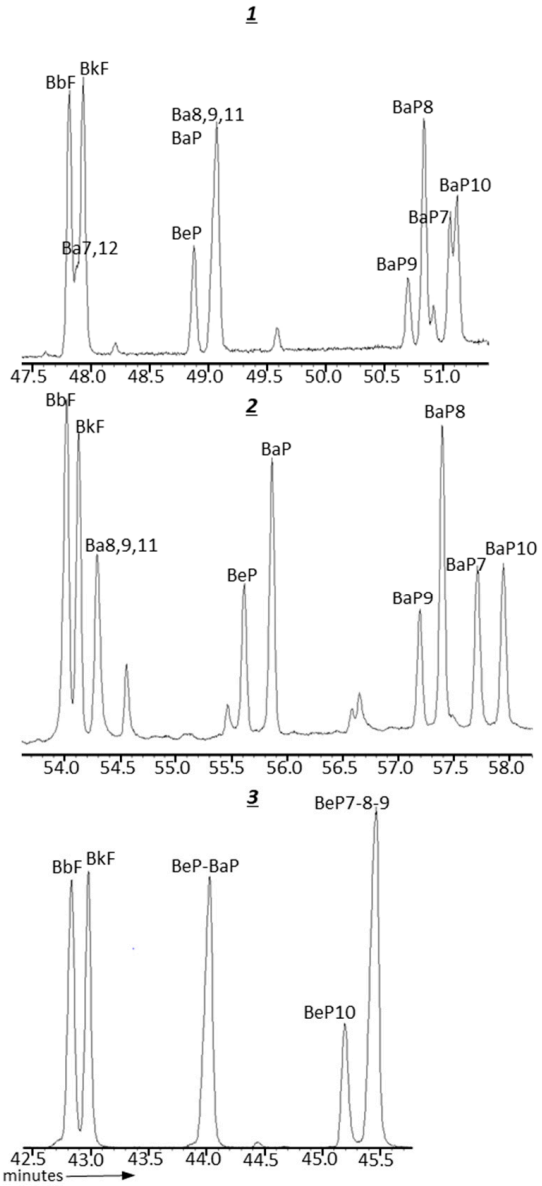

Figure 4. Elution order of benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*e*)pyrene, benzo(*a*)pyrene and methylbenzo(*a*)pyrenes on phenyl arylene (**1**), 50% phenyl-polysiloxane (**2**) and SLB-ILPAH (**3**) stationary phases. For abbreviations see Table 2.

Overlap of 3-methylbenz(*a*)anthracene with 5-methylbenz(*a*)anthracene and 4-methylbenz(*a*)anthracene with 6-methylbenz(*a*)anthracene was observed on all three columns (Figure 3). It is worth noting that these isomers could not be separated by GC×GC-MS with different column combinations either [29]. The DB-5 (60 m)×LC-50 (1.2 m) column combination tested by Skoczynska et al. [29] in the analysis of the 228-C1 methylated PAHs was able to separate in the second dimension 7-methylbenz(*a*)anthracene from 9-methylbenz(*a*)anthracene isomers, two

compounds that coelute on the DB-5ms and the 50% phenyl-polysiloxane. Significant differences in selectivity between the LC-50 and the Rxi-PAH (50% phenyl comparable to the SLB PAHms phase) were shown in the study of Nalin et al. [12]. The elution pattern of methylchrysenes (228-C1) and methylbenzo(*a*)pyrenes (252-C1) obtained on Rxi-PAH by Nalin et al. is similar to the pattern obtained on the 50% phenyl-polysiloxane in this study (even though Nalin et al. analysed more isomers). Coupling of LC-50 in the second dimension with 50% phenyl-polysiloxane in the first dimension could, therefore, result in orthogonal separation of the coeluting isomers (e.g. 7-methylbenz(*a*)anthracene from 9-methylbenz(*a*)anthracene). The SLB-ILPAH shows the strongest deviation in the retention pattern due to a different type of interactions between the analytes and the stationary phase than in the other two columns studied. Therefore, using this column together with 50% phenyl-polysiloxane may result in orthogonal separation of different PAHs isomers in one GC×GC run. Because of the "dual nature" of the IL columns, the coupling of a "standard" 50%-phenyl polysiloxane column with an IL column in a GC×GC analysis will almost certainly result in an improved separation of the PAHs isomers; a follow-up study may include the evaluation of ionic liquid stationary phases with different polarity coupled to a 50% phenyl-polysiloxane column.

Very little tailing was observed and the peak shapes obtained on all three columns were satisfactory (Figures 1–4). The variation in response obtained on the three columns was relatively small.

Figure 5 shows the column bleed of the three phases: the bleeding of the 50% phenyl-polysiloxane and the SLB-ILPAH phases were comparable and several times lower than the bleeding of the phenyl arylene "low bleed" stationary phase.

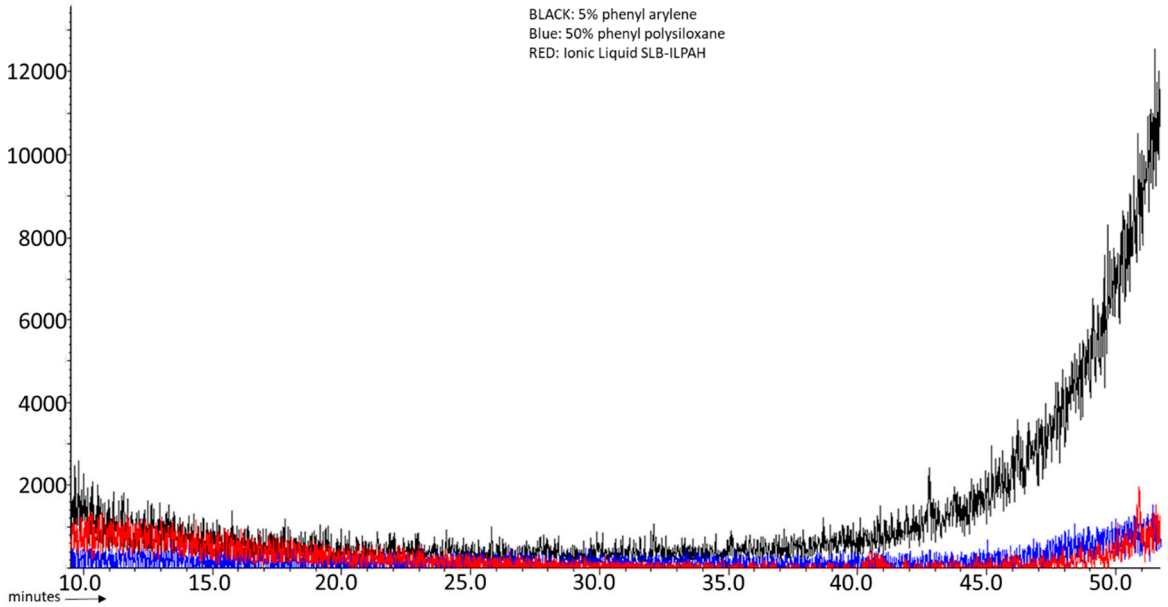

Figure 5. Bleeding of three columns (T max = 300): phenyl arylene (black), 50% phenyl-polysiloxane (blue) and SLB-ILPAH (red) stationary phases.

4. Conclusion

None of the three columns tested offers a complete separation of the injected PAH and methyl-PAH isomers. On the SLB-ILPAH column 22, isomers overlapped at more than 50% of the peak height. The phenyl arylene column showed an overlap of 19 isomers and the 50% phenyl-polysiloxane phase of 13 isomers. Also, none of the columns was able to totally resolve all 16 EPA PAHs. The 50% phenyl-polysiloxane column showed the best overall resolving power and is, therefore, currently considered the best option for the PAH and methyl-PAH analysis.

However, the SLB-ILPAH column is interesting because of a strongly deviating elution pattern, which is due to the different type of interactions between the analytes and the stationary phase.

That makes the ionic liquid column interesting for specific separations that cannot be obtained on one of the other two columns or possibly on other traditional phases. A huge advantage of the ionic liquid column is, for example, the total separation of chrysene from triphenylene. An additional advantage is that using this ionic liquid phase, together with e.g. the 50% phenyl-polysiloxane phase, may result in a (semi-)orthogonal separation of PAHs and methyl PAHs in one GC×GC run.

The ionic liquid SLB-ILPAH column and the high phenyl content 50% phenyl-polysiloxane column both show better thermal stability with less bleeding compared to that of the phenyl arylene "low bleed" column. This low bleeding is an asset for GC×GC because often, more polar columns are used, which show higher bleeding.

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