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Gas chromatographic retention behaviour of polychlorinated naphthalenes on non-polar, polarizable, polar and smectic capillary columns

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Abstract

Six commercially available gas chromatography columns were investigated for performance in separating polychlorinated naphthalenes (PCNs). Retention behaviour on the investigated phases is compared and retention data for 40 congeners on a 5% phenyl–methylpolysiloxane column is reported. For all columns, except the octylmethylpolysiloxane and the smectic, a relation between substitution pattern and retention was found, where substitution in adjacent positions as well as α-substitution increase the retention time. A mathematical model based on these findings was developed and used to predict the relative retention of all congeners from di- up to octachloronaphthalene, on a 5% phenyl–methylpolysiloxane column.

1. Introduction

Polychlorinated naphthalenes (PCNs) are two-ringed aromatic compounds substituted with chlorine atoms in one to eight positions, numbered as in Fig. 1. Positions 1, 4, 5, 8 and 2, 3, 6, 7 are sometimes referred to as α and β, respectively. Altogether 75 different structures are possible and it has not yet been established how many of these are present in technical formulations and in environmental samples. Table 1 lists all possible structures and some properties together with a number system. This numbering convention is consistent with that originally proposed for PCNs by Wiedmann and Ballschmiter [1].

PCNs exhibit similar physical properties as polychlorinated biphenyls (PCBs), i.e. excellent weathering resistance and electrical insulation properties and chemical and thermal stability.

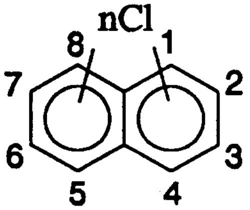

Fig. 1. Generalized structure of polychlorinated naphthalenes.

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Table 1
Numbering, properties and retention data of polychlorinated naphthalenes.

PCN number [a]		α-Cl	Substitution	B.p.[b]	M.p.[b]	Obs. t_R	Pred. t_R
Monochloronaphthalenes							
1		1	1-	259.3^{760}	−4 to 2.3		
2		0	2-	256	58–60		
Dichloronaphthalenes							
3	B	1	1,2-	295–298	34–37	1.089	1.089
4	B	1	1,3-	291^{775}	61.5–62	1.035	1.058
5	B	2	1,4-	$286–287^{740}$	68–72	1.055	1.055
6	B	2	1,5-	Subl.	106.5–107	1.062	1.055
7		1	1,6-	Subl.	48.5–49		1.055
8		1	1,7-	285–286	61.5–64		1.055
9	B	2	1,8-	Decomp.	88–89.5	1.181	1.181
10		0	2,3-		119.5–120.5		1.067
11	B	0	2,6-	285	135–141	1.060	1.060
12	B	0	2,7-		114–116	1.060	1.060
Trichloronaphthalenes							
13	B	1	1,2,3-		81–84	1.414	1.398
14		2	1,2,4-		92		1.371
15	B	2	1,2,5-		74–79	1.363	1.371
16	B	1	1,2,6-		90–92.5	1.370	1.366
17	B	1	1,2,7-		88	1.388	1.366
18	B	2	1,2,8-		83	1.388	1.436
19		2	1,3,5-		102–103		1.315
20	B	1	1,3,6-		80.5–81	1.291	1.310
21	B	1	1,3,7-		112.5–113	1.309	1.310
22	B	2	1,3,8-		89.5	1.444	1.379
23		3	1,4,5-		130–131		1.384
24	B	2	1,4,6-		65–68	1.317	1.315
25		1	1,6,7-		109–109.5		1.342
26	B	0	2,3,6-		90–91	1.393	1.393
Tetrachloronaphthalenes							
27	B	2	1,2,3,4-		196–198	1.787	1.820
28	B	2	1,2,3,5-		141	1.745	1.745
29		1	1,2,3,6-				1.754
30	B	1	1,2,3,7-		115	1.775	1.754
31	N	2	1,2,3,8-		128		1.941
32		3	1,2,4,5-				1.824
33	B	2	1,2,4,6-		111	1.641	1.637
34		2	1,2,4,7-		140–144		1.637
35		3	1,2,4,8-				1.824
36		2	1,2,5,6-		164		1.711
37		2	1,2,5,7-		114		1.637
38		3	1,2,5,8-				1.824
39		1	1,2,6,7-				1.754
40		2	1,2,6,8-		125–127		1.832
41		2	1,2,7,8-				1.907
42	B	2	1,3,5,7-		178–181	1.562	1.562
43	B	3	1,3,5,8-		131	1.746	1.749
44	B	1	1,3,6,7-		119–120	1.679	1.679

Table 1 (*continued*)

PCN number [a]		α-Cl	Substitution	B.p.[b]	M.p.[b]	Obs. t_R	Pred. t_R
Tetrachloronaphthalenes cont.							
45		2	1,3,6,8-				1.758
46	*B*	4	1,4,5,8-		183	1.936	1.936
47	*B*	2	1,4,6,7-		139	1.692	1.670
48		2	2,3,6,7-		135		1.796
Pentachloronaphthalenes							
49		3	1,2,3,4,5-		168.5		2.352
50		2	1,2,3,4,6-		147		2.151
51		2	1,2,3,5,6-				2.151
52	B	2	1,2,3,5,7-		171	2.050	2.033
53	N	3	1,2,3,5,8-		174–176		2.234
54		1	1,2,3,6,7-				2.199
55	N	2	1,2,3,6,8-		112–114		2.267
56	N	2	1,2,3,7,8-		115–117		2.385
57	N	3	1,2,4,5,6-		136–139		2.219
58		3	1,2,4,5,7-				2.101
59	N	4	1,2,4,5,8-		150–151		2.302
60		2	1,2,4,6,7-				2.033
61		3	1,2,4,6,8-		135		2.101
62		3	1,2,4,7,8-				2.219
Hexachloronaphthalenes							
63	N	3	1,2,3,4,5,6-		132–134	2.809	2.809
64	N	3	1,2,3,4,5,7-		164–166	2.655	2.647
65	N	4	1,2,3,4,5,8-		163.5–164.5	2.861	2.861
66		2	1,2,3,4,6,7-		205–206	2.589	2.589
67		2	1,2,3,5,6,7-		234–235	2.589	2.589
68	N	3	1,2,3,5,6,8-		153–154	2.655	2.647
69	N	3	1,2,3,5,7,8-		148–149	2.679	2.647
70	N	2	1,2,3,6,7,8-		158–160	2.886	2.886
71		4	1,2,4,5,6,8-		175–177	2.705	2.705
72		4	1,2,4,5,7,8-		136–137	2.705	2.705
Heptachloronaphthalenes							
73		3	1,2,3,4,5,6,7-			3.250	3.310
74		4	1,2,3,4,5,6,8-		194	3.265	3.368
Octachloronaphthalene							
75		4	1,2,3,4,5,6,7,8-		197.5–203	3.981	4.030

Relative retention times were determined on a 5% phenyl–methylpolysiloxane column (HP Ultra 2, 50 m) and calculated relative to pentachlorobenzene (1.000).

[a] B denotes standards obtained from Prof. Udo A. Th. Brinkman. N, identity/property is according to Nikiforov [2].

[b] ????????

Therefore technical formulations under trade names such as Halowax (Koppers Company Inc., Pittsburgh, PA, USA), Nibren Wax (Bayer, Leverkusen, Germany), Seekay Wax (Imperial Chemical Industries, Manchester, UK) and Clonacire Wax (Prodelec, Paris, France) have found numerous applications such as dielectrics in capacitors, sealant for electrical equipment, oil additive, wood preservative and impregnating agent for paper and textile [3]. Apart from deliberate production and leakage to the environment as a result of careless use, PCNs are also released to the environment through the use of PCBs, due to its presence as a micro-contaminant in technical PCB formulations [4]. Several high-temperature processes such as waste incineration and metal reclamation have also been found to produce PCNs [5–7].

PCNs were recognized as early as 1939 as toxic compounds when cases of occupational exposure resulted in the death of several workers in capacitor factories [8]. General toxicological effects exhibited by PCNs are skin defects (chloracne among exposed humans, hyperkeratosis among exposed animals) and liver damage. Chloracne and liver damage have been found to be more pronounced with the higher chlorinated PCNs, i.e. penta- and hexachlorinated naphthalenes [3]. Some of the hexa- and heptachlorinated naphthalenes have been studied in enzyme induction tests; EROD (7-ethoxyresorufin-*o*-deethylase) and AHH (aryl hydrocarbon hydroxylase) enzyme induction. These results indicated a TCDD-like toxicity of two to three orders of magnitude less than 2,3,7,8-tetrachlorodibenzo-*p*-dioxin [9].

Long-term release to the environment in combination with persistency of this substance group, has lead to PCNs being a ubiquitous pollutant. Levels of total PCNs in background biota have been reported ranging from 0.03 to 2 ppb measured on a lipid weight basis [10–13].

PCN levels are commonly reported as total PCNs rather than on an individual congener basis, due to lack of pure reference substances as well as difficulties in achieving a complete congener separation. Only a few investigations have reported levels of individual peaks according to their elution order on a specific column. The results of these investigations show that some congeners appear to be preferentially retained in biota. These constitute the first eluting peak of each homologue group on a 5% phenyl–methylsilylated GC column and have the same retention times as the following congeners; 1,3,5,7-tetrachloronaphthalene; 1,2,3,5,7-pentachloronaphthalene; 1,2,3,4,6,7- and 1,2,3,5,6,7-hexachloronaphthalene (coeluting) and 1,2,3,4,5,6,7-heptachloronaphthalene [13–16].

Brinkman and co-workers [17–19] have previously reported extensive chromatographic data on different liquid chromatographic systems for most of the lower chlorinated congeners included in this investigation. Beland and Geer [20] studied the gas chromatographic separation on two packed columns; 10% Carbowax on 60–80 mesh Chromosorb W and 5% Bentone34–10% OV-101 on 100–120 mesh Supelcoport and reported data for 20, mainly lower chlorinated congeners.

Chromatographic separation of polychlorinated naphthalenes as a group has been successfully accomplished on a high resolution gel permeation column [4]. To a certain extent, PCNs may be separated from the bulk of PCBs together with non-planar PCBs on a 2-(1-pyrenyl)-ethyl(dimethyl)silylated (PYE) silica HPLC column [21]. On this type of column the successful separation of two hexachloronaphthalenes (1,2,3,4,5,6- and 1,2,3,5,6,7-hexachloronaphthalene) has been reported [16].

The primary aims of the present investigation were to find a set of GC columns that separate as many congeners as possible in order to be able to determine specifically the environmentally more persistent ones and especially the two previously mentioned hexachloronaphthalenes, and secondly, to investigate the general versatility of different stationary phases in use for analysis of halogenated polycyclic aromatic compounds (XPAC).

2. Experimental

2.1. Chemicals

Halowax 1014 (a technical mixture with approximately 62% chlorine content) was a gift from Koppers Company Inc., Pittsburgh, PA, USA. Of the individual polychlorinated naphthalene standards, all di- to pentachloronaphthalenes used in this investigation (labelled

B in Table 1) were a generous gift from Prof. Udo A. Th. Brinkman, Free University, Amsterdam. The synthesis of these substances and their data were published previously [17]. 1,2,3,4,6,7-, 1,2,3,5,6,7-, 1,2,4,5,6,8-, 1,2,4,5,7,8-hexa, 1,2,3,4,5,6,7-hepta-, and octachloronaphthalene were synthesized as described previously [16,22]. Pentachlorobenzene was a kind gift from Prof. Carl-Axel Wachtmeister at the Wallenberg Laboratory, Stockholm University.

2.2. Columns

Columns were selected to represent stationary phases having different polarities, or exhibiting interactions related to solute geometry, i.e. length-to-breadth ratio and planarity. A column with 5% phenyl–methylpolysiloxane on carborane was also included as this phase, according to Rotzsche [23], has a quasi-aromatic structure that we expected could exhibit specific electron donor–acceptor interactions.

Table 2 lists the investigated columns together with their characteristics.

2.3. Instrumentation

Gas chromatography was performed on a Hewlett Packard 5890 gas chromatograph equipped with a split/splitless injector and a Hewlett Packard 5970B mass selective detector operated in the selected-ion monitoring mode (SIM). Ions from di- up to heptachloronaphthalene were monitored throughout the chromatogram (196, 230, 264, 300, 334 and 368 amu).

Carrier gas was helium 99.995% with all columns, and standard settings for column head pressure were used according to column dimensions.

Temperature programs were established through the injection of approximately 120 ng of

Table 2
Column characteristics

Column name	Manufacturer	Stationary phase	Dimensions (length × I.D.)	Film thickness (μm)	Character
Ultra 1	Hewlett Packard	Dimethylpolysiloxane	50 m × 0.32 mm	0.32	non-polar
Ultra 2	Hewlett Packard	5% Phenyl–dimethyl polysiloxane	50 m × 0.20 mm	0.33	low-polar/ polarizable
HT 5	Scientific Glass Engineering	5% Phenyl–dimethyl polysiloxane on carborane	25 m × 0.22 mm	0.10	low-polar/ quasi-aromatic
CP-Sil 88	Chrompack	100% Cyanopropyl–polysiloxane	50 m × 0.32 mm	0.32	polar
SB-Octyl 50	Lee Scientific	50% *n*-Octyl–dimethyl polysiloxane	50 m × 0.20 mm	0.25	non-polar/ structural interactions
SB-Smectic	Lee Scientific	Biphenylcarboxylate ester methylpolysiloxane	25 m × 0.32 mm	0.15	medium-polar/ structural interactions

Table 3
Instrument parameters

Column	Injector/detector temp (°C)	Injector pressure (hPa)	Temperature program temp(time)/rate
HP Ultra 1	280/290	180	90(2)–200/25–290(36.6)/2
HP Ultra 2	280/290	180	90(2)–200/25–290(36.6)/2
HT5	290/290	90	90(2)–200(2)/15–290(9.3)/2
CP-Sil 88	240/240	180	90(2)–150(2)/15–230(6)/2
SB-Octyl	280/290	180	90(2)–200(2)/20–270(7.5)/1.5
SB Smectic	250/250	90	90(2)–150(2)/10–180(8)/2–230(25)/1.5

Halowax 1014. When and if a satisfactory separation was achieved for Halowax 1014, individual PCN standards were injected together with pentachlorobenzene as retention time reference, and relative retention times were established. Thus, individual standards were analysed only on the most promising columns. GC settings and temperature programs are listed in Table 3.

3. Results and discussion

3.1. General performance

None of the investigated columns was able to resolve all PCN congeners as single peaks. Neither did any of them separate the two hexachloronaphthalenes (1,2,3,4,6,7- and 1,2,3,5,6,7-hexaCN). According to Williams et al. [24] this separation was unsuccessful on several other columns as well. Table 4 lists the number of resolved peaks in Halowax 1014 in each homologue group for the columns in the present investigation (in this text resolved refers to a valley at half the peak height of the smaller peak, which is normally handled by chromatographic data systems). For comparison, the total number of congeners in each homologue group is also given in the table. It should be noted that a strict comparison between some of the columns is not appropriate, due to differing column lengths. Our view is that four columns were more versatile for PCN analysis than the others, namely 5% phenyl–methylpolysiloxane (HP Ultra 2), 50% octyl–methylpolysiloxane (SB-Octyl), 100% cyanopropylpolysiloxane (CP-Sil 88) and the smectic phase (SB Smectic).

On the non-polar dimethylpolysiloxane column (HP Ultra 1), PCNs of different homologue groups eluted as distinctly separated clusters. Increasing the polarity of the column phase yielded an increased resolution within each

Table 4
Comparison of column versatility

Column name	Number of resolved peaks					
	di-CN	tri-CN	tetra-CN	penta-CN	hexa-CN	hepta-CN
Total no.	10	14	22	14	10	2
Ultra-1	5	8	13	11	6	1
Ultra-2	5	8	12	11	6	2
HT5	5	7	13	10	6	1
Cp-Sil 88	3	7	12	10	6	2
SB-Octyl	4	6	12	9	7	2
SB-Smectic	3	7	11	8	6	2

homologue group as illustrated in Fig. 2a and b. A further increase in polarity led to the different homologue groups sliding into each other (Fig. 2c).

The 5% phenyl–methylpolysiloxane column (HP Ultra 2) clearly separated PCNs of different homologue groups showing no difficulties with overlap.

The 5% phenyl–methylpolysiloxane on carborane (HT 5) did not seem to exhibit any separation characteristics different from the other 5% phenyl–methylpolysiloxane column.

On the 50% octyl–methylpolysiloxane column (SB Octyl) PCNs eluted in rather distinct groups according to their chlorine content in much the same way as on the dimethylpolysiloxane column. Several peaks appeared reversed on this column and among the hexachloronaphthalenes one more peak was resolved, presumably one of 1,2,3,4,5,7- or 1,2,3,5,6,8-hexaCN. This may indicate the presence of an additional interaction as compared to the other non-polar column. However, this column did not show any specific retention of the 1,3,5,7-tetraCN, 1,2,3,5,7-pentaCN and the 1,2,3,5,6,7-hexaCN which may be expected to be more planar than the other congeners. This leads to the conclusion that the interaction related to planarity, as suggested by Fischer et al. [25] on this type of column, is not strong enough to exhibit the same difference between PCN congeners as that found between non-ortho- and ortho substituted PCBs.

The 100% cyanopropylpolysiloxane column (CP Sil 88) exhibited more resolution within each homologue group as illustrated previously. Total number of resolved peaks was similar to the other columns but the first pentachloronaphthalene peak was resolved into two, of which the first one is expected to be the 1,2,4,6,7-pentaCN and the second is tentatively identified as the 1,2,3,5,7-pentaCN. In a sample of Guillemot egg from the Baltic, analysed on this column, two pentaCN peaks were present at the same retention times as the two previously mentioned pentaCN showing that these are present in the environment. As previously illustrated in Fig. 2c, considerable overlap of homologue groups on this column, and especially with the tetrachloronaphthalenes into the pentachloronaphthalenes, may cause difficulties in peak assignment, and when quantifying as fragment ions may interfere with molecular ions from lower chlorinated species.

The smectic column (SB Smectic) exhibited some overlap between homologue groups. This column was found to change its selectivity to PCNs drastically when modifying the temperature program and it seemed important to optimize the temperature program according to the separation needs. It was possible to obtain separation between two additional hexachloronaphthalenes 1,2,4,5,6,8-, and 1,2,4,5,7,8-hexaCN, though some resolution was then lost among the lower chlorinated congeners. With this phase the retention order was completely different from the other phases indicating the presence of a different type of interaction. This column specimen showed some problem with peak distortion, especially with the relatively high sample load required to analyse the minor PCN peaks in Halowax 1014.

3.2. Retention mechanisms

All columns investigated, except the SB-octyl and the SB-smectic, exhibited essentially the same retention order within each homologue group indicating that the retention behaviour on these columns relates to the same property of the PCN congeners. Apart from a general increase in the retention with increasing number of chlorine substituents, the position of the substituent is of great importance. The following observations were all connected with an increased retention; 1) increasing number of α-chlorines 2) increasing number of chlorines substituted in adjacent positions, the effect increasing in the order; $\alpha\beta$; $\beta\beta$; $\alpha\alpha$, 3) an uneven distribution of chlorine substituents between the rings and 4) the occurrence of 2,6-substitution. This behaviour is illustrated by the elution order of the dichloronaphthalenes:

1,3 < 1,4 < 1,5 & 2,6 & 2,7 < 1,2 < 1,8

The elution order of all the investigated standards, on a 5%phenyl–methylpolysiloxane column, is given in Table 5.

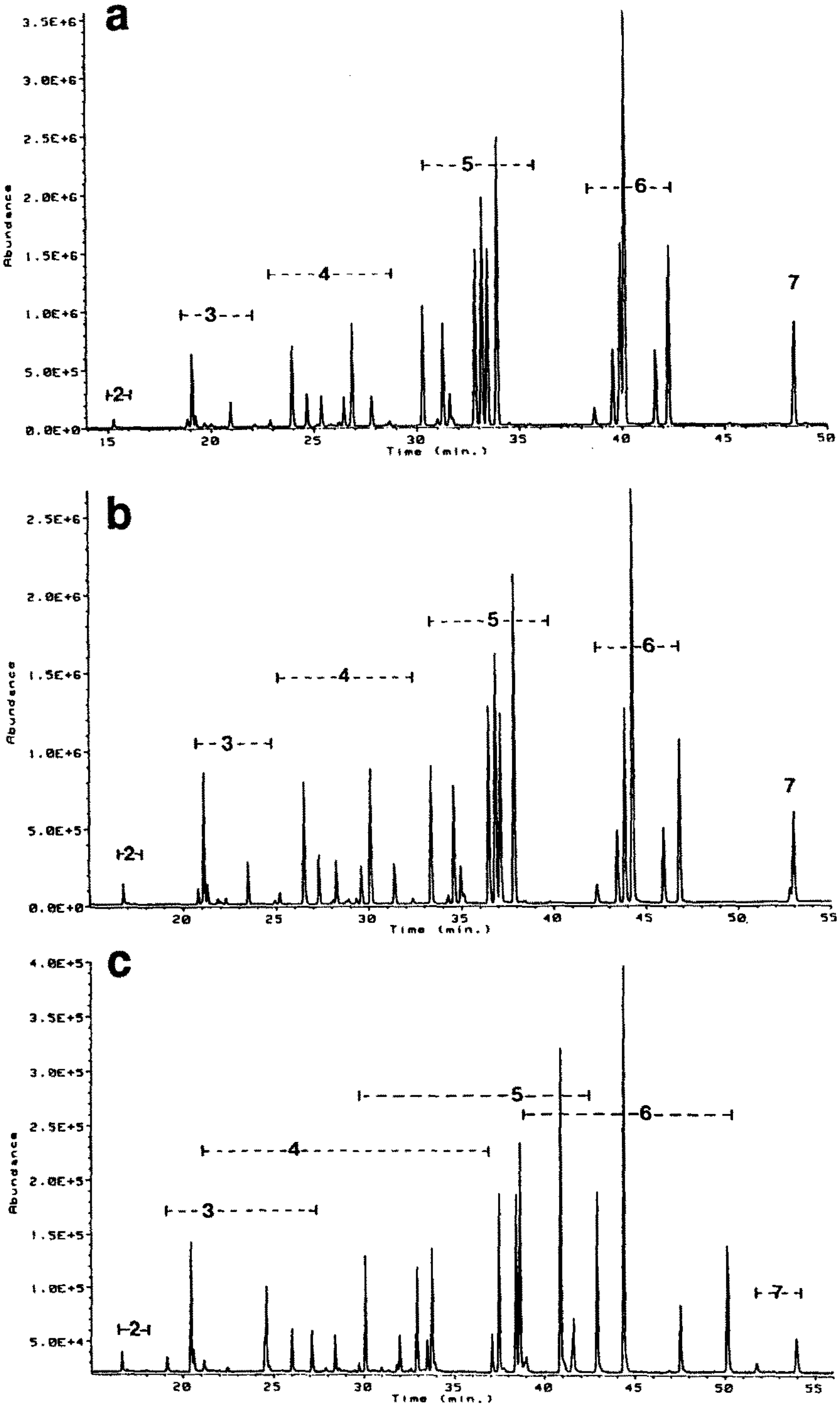


Fig. 2. Total ion chromatograms of technical PCN mixture Halowax 1014 on (a) dimethylpolysiloxane (HP Ultra 1, 50 m), (b) 5% phenyl–methylpolysiloxane (HP Ultra 2, 50 m) and (c) 100% cyanopropylpolysiloxane (CP-Sil 88, 50 m). Details on these columns are given in Table 2, and temperature programs in Table 3.

Table 5
Comparison of retention order on two different phases.

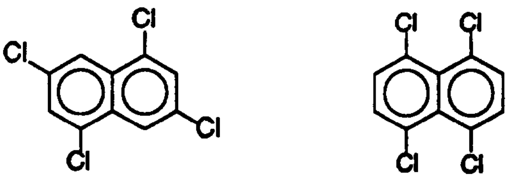
5% Phenyl–methylpolysiloxane	Smectic
Dichloronaphthalenes	
	1,4-
1,3-	1,3-
1,4-	1,5-
1,5-; 2,6-; 2,7-	2,7-
1,2-	1,2-
1,8-	1,8-
	2,6-
Trichloronaphthalenes	
1,3,6-	1,4,6-
1,3,7-	1,3,6-
1,4,6-	1,2,5-
1,2,5-	1,2,7-
1,2,6-	1,2,3-
1,2,7-; 1,2,8-	1,2,8-
2,3,6-	1,3,8-
1,2,3-	1,2,6-
1,3,8-	2,3,6-
Tetrachloronaphthalenes	
1,3,5,7-	1,3,5,7-
1,2,4,6-	1,2,4,6-
1,3,6,7-	1,4,6,7-
1,4,6,7-	1,3,5,8-
1,2,3,5-; 1,3,5,8-	1,3,6,7-
1,2,3,7-	1,2,3,5-
1,2,3,4-	1,2,3,4-
1,4,5,8	1,2,3,7-
	1,4,5,8-
Hexachloronaphthalenes	
1,2,3,4,6,7-, 1,2,3,5,6,7-	1,2,3,4,6,7-; 1,2,3,5,6,7-
1,2,3,4,5,7-, 1,2,3,5,6,8-	1,2,3,5,7,8-
1,2,3,5,7,8-	1,2,3,4,5,7-; 1,2,3,5,6,8-
1,2,4,5,6,8-, 1,2,4,5,7,8-	1,2,4,5,6,8-; 1,2,4,5,7,8-,
	Resolved in two peaks
1,2,3,4,5,6-	1,2,3,6,7,8-
1,2,3,6,7,8-	1,2,3,4,5,6-
Heptachloronaphthalenes	
1,2,3,4,5,6,7	1,2,3,4,5,6,8-
1,2,3,4,5,6,8-	1,2,3,4,5,6,7-

Brinkman et al. [18] previously reported a strong relation between adjacent substitution and increased retention for di- and tetraCN in liquid chromatography using the system silica–*n*-hexane for the lower chlorinated PCN congeners. They reported that especially the 1,8-, 2,3-, di- and 1,4,5,8-tetraCN congeners were strongly retained compared with 1,4-, 1,5-, di- and 1,3,5,7-tetraCN congeners.

The observations on adjacent substitution seem to hold for several other substituted aromatics as well such as polychlorobenzenes [26], ethyl- and trimethylbenzenes [27] and polychlorinated dibenzofurans [28]. This may be the case for polychlorobiphenyls as well though the relation is complicated by the fact that these molecules are not rotationally fixed. The last eluting PCB congeners in each homologue group, on a 5% phenyl–methylpolysiloxane column, are in fact the 3,3′4,4′-tetra-, 3,3′4,4′5-penta- and 3,3′4,4′5,5′-hexachlorobiphenyls all substituted in adjacent positions [29].

The observation of the relative importance of $\alpha\alpha$-substitution agrees with investigations on other substance groups and corresponding positions. In the data of Hale et al. [28], 1,9-substituted dibenzofurans are the last eluting congeners within each homologue group. For PCBs, however, which are free to rotate around the biphenyl bridge bond, substitution in the 2,2′-positions results in a deviation from planarity causing a decreased retention on 5% phenyl–methylpolysiloxane column [29].

Considering the non-polar dimethylpolysiloxane column as separating according to the boiling point or more strictly to vapour pressure, the observed retention behaviour indicates that solute–phase and solute–solute interactions are based on the same property of the PCNs. Increasing polarity is generally associated with increasing boiling point. However, both 1,3,5,7-tetrachloronaphthalene on the one hand and 1,4,5,8-tetrachloronaphthalene on the other hand are expected to lack an overall dipole



1,3,5,7-TCN **1,4,5,8-TCN**

Fig. 3. Tetrachloronaphthalenes with an "even" and "uneven" chlorine substitution, respectively.

moment (Fig. 3). Nevertheless, the latter one is strongly retained compared to the former one. However, the unevenly substituted 1,4,5,8-tetrachloronaphthalene may be considered to have regions where the delocalized electron density is decreased as well as regions where electron density is enhanced. These regions may result in orientation forces between solute–solute and solute–phase molecules.

Lee et al. [30] introduced the terminology of centres of positive or negative charge concerning polarizable stationary phases such as phenyl–methylpolysiloxane and this terminology may be adequate for the discussed polychlorinated naphthalenes as well. Thus, it seems likely that separation of PCNs on non-polar, polarizable and polar phases rests mainly on interactions related to some polar property of the individual congener.

As mentioned previously, the retention behaviour was more complicated on the smectic column. In addition to the previously discussed interactions that may relate to π-electrons of the biphenyls of the smectic phase, a retention based on molecular geometry of the solute may be present as suggested by several authors [31–33]. Markides et al. [32] described the separation mechanism on this type of phase as a combination of retention related to length-to-breadth ratio and planarity as well as Van der Waals interactions. Nishioka et al. [33] found a relation between retention and length-to-breadth ratio L/B for polycyclic aromatic compounds. Compounds with a high L/B were more retained than those with a low ratio. This seems to hold also for PCNs. Table 5 is a comparison of retention order between a 5% phenyl–methylpolysiloxane (HP Ultra 2) column and the smectic column. It can be seen, for instance, that the 1,4- substituted di- tri- and tetrachloronaphthalenes tend to elute earlier on the smectic column than on the 5% phenyl–methylpolysiloxane column while the "longer" 2,6- substituted di- and trichloronaphthalenes are correspondingly more retained.

It is possible to assess a quantitative relationship between substitution pattern and retention so that the retention order can be predicted. Hale et al. [28] proposed a model for predicting retention indices for polychlorinated dibenzofurans. The model is derived truly empirically and accounts for the number and position of chlorine substituents as well as intra- and inter-ring effects of different substituents. Naphthalene is, however, a fused polycyclic aromatic molecule and may be expected to behave somewhat differently from dibenzofuran derivatives. We therefore developed a new model based on the above findings. Using the retention data from the 5% phenyl–methylpolysiloxane (HP Ultra 2) column in the present investigation, a model was set up describing the relation between substitution pattern and relative retention (*rrt*) on this column. The model assumes full additivity and has the following general appearance:

$$rrt = Ax + By + Cz + Du + Ev$$

where x, y, z, u, v are the number of chlorines or pairs with the respective $\alpha(A)$, $\beta(B)$, adjacent $\alpha\beta(C)$, adjacent $\alpha\alpha(D)$, adjacent $\beta\beta(E)$ substitution. The coefficients A, B, C, D and E were obtained by solving equations describing the relation between substitution pattern and relative retention for the standard substances of four homologue groups. Thus four sets of coefficients were calculated (di-, tri-, tetra- and hexachlorinated). These coefficients were further optimized to minimize the residual sum of squares between observed and predicted relative retention times using the Newtonian search algorithm in the personal computer package Solver (a module in Microsoft Excel).

In Table 1 the observed and predicted relative retention times for di- up to hexachlorinated naphthalenes are given. Predicted relative retention times for hepta- and octachloronaphthalenes were calculated using coefficients for hexachloronaphthalenes.

The model is based on a selection of congeners available and may not be fully representative since some critical congeners are missing, i.e. 2,3,6,7-tetraCN. With few exceptions however, the predicted and observed values follow closely and the predicted order is mostly correct.

One major objective for the development of the retention time model was to provide a hint on the identities of several of the unknown peaks present in Halowax and in environmental samples. Special attention was drawn to the pentachloronaphthalenes since very few of these are available as pure standards. Therefore, coefficients for the pentaCN were interpolated from those of tetra- and hexachloronaphthalenes and relative retention times were calculated. It appears that, even though predicted values are somewhat off scale from the relative retention of the observed pentaCN peaks, the predicted elution order seems reasonable. In order to test and develop the model for the pentaCN, several congeners with different substitution are needed.

4. Conclusions

This investigation indicates that a full congener separation requires the involvement of several different molecular properties. At present, a combination of liquid chromatography and the most versatile gas chromatographic columns can resolve approximately 60 congeners. From the experience of previous results and the present investigation it can be expected that the number of PCN congeners actually present in the technical mixture Halowax 1014 and in the environment exceeds 60. The retention time model developed in this investigation may be a useful tool in search for the presently unknown identities of several PCN peaks found in the technical mixture Halowax 1014 and in environmental samples. The predicted relative retention times for pentachloronaphthalenes suggest that the identity of one of the persistent pentaCN found in Baltic Guillemot egg may be the 1,2,4,6,7-pentaCN.

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