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ANALYSIS OF POLYCHLORINATED NAPHTHALENES BY HIGH-PERFORMANCE LIQUID AND THIN-LAYER CHROMATOGRAPHY

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SUMMARY

High-performance liquid chromatography (HPLC) in the system silica gel–dry *n*-hexane has been used to characterize the behaviour of several series of commercially available mixtures of chlorinated naphthalenes, *viz.*, Halowax 1031–1051, Clonacire 90–130 and Nibren D88–D130. A large number of peaks in the chromatograms of the Halowaxes have been assigned to individual constituents. To this end, retention times and UV spectra have been recorded for 33 polychlorinated naphthalenes. The dependence of retention and spectral characteristics on the number and position of the chlorine atoms in the naphthalene nucleus is discussed. The results of HPLC are compared with those obtained with several normal and reversed-phase thin-layer chromatographic systems.

INTRODUCTION

In recent years, a large number of papers and reviews has been devoted to the chemistry, analysis, environmental hazards, etc., of polychlorinated biphenyls (PCBs). Much less attention has been paid to the study of polychlorinated naphthalenes (PCNs), although according to one group[1] their production may amount to about 10% of that of PCBs. Recently, it has been shown[2] that next to gas–liquid chromatography (GLC), high-performance liquid chromatography (HPLC) is a powerful technique for the identification and quantitative analysis of PCBs. As a continuation of this work, in this paper the behaviour of PCNs in HPLC is reported, means for discriminating between PCNs and PCBs are discussed, and HPLC results are compared with those obtained by thin-layer chromatography (TLC), in both its normal and reversed-phase modes. The literature on chromatographic methods of analysis of PCN mixtures is briefly discussed below.

An extensive study on the identity of PCNs present in Halowax 1031, 1000, 1001 and 1099 was made by Beland and Geer[1]. From gas chromatograms run on two different columns, they concluded that both monochloronaphthalenes are present, together with all of the disubstituted isomers except 2,6-dichloronaphthalene, and with several of the possible tri- and tetrasubstituted isomers. At least three components appeared to be present that did not seem to be PCNs.

Stalling and Huckins[3] resolved the components of Halowax 1099, 1013 and 1014 by TLC in the system Kieselguhr impregnated with paraffin oil/water–acetone–acetonitrile–methanol (1:3:8:8). Next, the spots were eluted with light petroleum containing 5% of diethyl ether, and analyzed by GLC on a column of 0.3% OV-7 on glass beads. There appeared to be a general tendency for PCNs with higher chlorine contents to display lower R_F values.

Goerlitz and Law[4], who demonstrated that PCNs may interfere with the GLC analysis of common pesticides, reported the presence of about 10 major peaks in Halowax 1013 and 1014, attributable to tri- to hexa- (and hepta-; Halowax 1014 only) chloronaphthalenes. They recommended the use of GLC–MS as an excellent method to distinguish between PCNs, pesticides and PCBs. Alternatively, one can process each sample through a scheme such as that detailed by Armour and Burke[5,6], according to whom a silica gel column chromatographic procedure gives a favourable separation of all Halowaxes tested from most of the common organochlorine pesticides.

Gulan *et al.*[7] trapped the PCNs as they were eluted from the gas chromatograph, exposed them to UV radiation and re-chromatographed the component peaks and their products. Characteristic degradation patterns were observed, which greatly facilitated the discrimination between PCNs (Halowax 1014) and several common pesticides and PCBs (Aroclor 1254). The minimal time that yielded about equal areas for the main degradation peak and for the parent peak was between 5 and 300 sec for the 12 component peaks of Halowax 1014.

In order to simplify the analysis of a heterogeneous mixture of PCNs and similar compounds, conversion into a single derivative has repeatedly been suggested. Usually, perchlorination is the preferred technique, especially on account of the high sensitivity of the electron-capture detector towards highly chlorinated compounds. Hutzinger *et al.*[8] carried out perchlorination by heating the PCN mixture, under reflux, with SO_2Cl_2–$SbCl_5$ (9:1) for 1 h. Octachloronaphthalene was obtained in good yield. Alternatively, treatment with a mixture of S_2Cl_2, SO_2Cl_2 and $AlCl_3$ and subsequent heating at a temperature exceeding 208° in order to convert the initially formed decachloro-1,4-dihydronaphthalene into octachloronaphthalene can be recommended. Zimmerli[9] determined PCBs, PCNs and other environmental contaminants by so-called carbon skeleton chromatography on a deactivated palladium catalyst. Under suitable conditions, PCBs were converted quantitatively into biphenyl. With PCNs, naphthalene was the main product; however, some tetralin was also formed.

EXPERIMENTAL

Materials

The PCN samples investigated include the complete Halowax series produced by Koppers (Pittsburgh, Pa., U.S.A.) and purchased through Analabs (North Haven, Conn., U.S.A.), three Clonacire and three Nibren samples, obtained as gifts from Prodelec (Paris, France) and Bayer (Leverkusen, G.F.R.), respectively. Their characteristics are summarized in Table I.

1,4-, 1,6- and 1,7-dichloronaphthalene were prepared from 1,4-dinitro-, 1,6-dinitro- and 2-amino-8-nitronaphthalene, respectively. Approximately 250 mg of starting material are refluxed for several hours in the presence of 750 mg of finely

TABLE I

CHARACTERISTICS OF COMMERCIALLY AVAILABLE PCN MIXTURES

Type	*Melting or softening point (°C)**	*Approx. Cl content (wt.-%)**	$\lambda_{max.}$**	
			B_b band	*L_a band*
Halowax				
1031	−25	22	224	274, 284
1000	−33	26	224	284, 292
1001	93	50	233	297, 304
1099	102	52	233	298, 305
1013	120	56	238	306
1014	137	62	244	310
1051	185	70	275	332
Clonacire				
90	90	—	233	295, 304
115	115	—	238	297, 305
130	130	—	238	306
Nibren				
D88	90	50	233	296, 304
D116N	113	—	238	306
D130	135	59	244	313

* Data from refs. 10–12.

** This work.

powdered tin and 8 ml of 6 *N* hydrochloric acid per nitro group present. The reaction mixture is extracted twice with 10 ml of diethyl ether and the aqueous phase is neutralized with sodium hydroxide and immediately extracted several times with diethyl ether. The ether extract is evaporated to dryness at room temperature. A 50-mg amount of the product is dissolved in 2 ml of 6 *N* hydrochloric acid and the solution is mixed with an ice-cold aqueous solution of 25 mg of sodium nitrite (per amino group present); after 5 min, some urea is added and the foam is broken by adding a few drops of diethyl ether. A solution of 30 mg of copper(I) chloride in 1 ml of concentrated hydrochloric acid (per amino group present) is added and the mixture is heated for 30 min on a steam-bath. After cooling, the polychloronaphthalene is extracted with 2 ml of *n*-hexane.

Milligram amounts of all other PCNs used in the present study were obtained as gifts from Dr. B. D. Geer (Montana State University, Bozeman, Mont., U.S.A.), through the courtesy of Dr. S. O. Farwell (Washington State University, Pullman, Wash., U.S.A.). 1- and 2-monochloronaphthalene were purchased from Fluka (Buchs, Switzerland); 1,2-dichloronaphthalene and 1,2,3,4-tetrachloronaphthalene were obtained from CPL (College Point, N.Y., U.S.A.) and Aldrich Europe (Beers, Belgium), respectively. Octachloronaphthalene was a product from Analabs.

Methods

A Siemens S100 liquid chromatograph equipped with an automatic injection system (10 μl) and a Zeiss PM2 DLC UV detector was used for HPLC. The column was a stainless-steel tube, 25 cm × 3 mm I.D., pre-packed with 5-μm LiChrosorb SI 60 silica gel (Merck, Darmstadt, G.F.R.). *n*-Hexane (ChromAR, Mallinckrodt, St.

Louis, Mo., U.S.A.), dried over molecular sieve 5A, was used as the mobile phase. The column was thermostatted at a temperature of 27 ± 1°.

Normal TLC was carried out in the system silica gel/*n*-hexane, using precoated silica gel plates (Kieselgel$_{254}$, Merck) activated overnight at 150°, and *n*-hexane (ChromAR, Mallinckrodt), dried over molecular sieve 5A. Development was effected in a sandwich chamber for a length of run of 10 or 20 cm, which takes *ca.* 20 min and 1 h, respectively. Detection was effected under UV light. Reversed-phase TLC was carried out on Kieselguhr (Kieselguhr G, Merck) impregnated with paraffin oil. Acetonitrile–methanol–acetone–water (20:20:9:1) and acetonitrile–methanol–water (8:9:3) were used as mobile phases. Development in a saturated chamber for a length of run of *ca.* 18 cm takes 1 h. After drying, the plates were sprayed with a solution of 0.5% tolidine in 80% ethanol containing 0.5% of glacial acetic acid. Blue or blue-green, and occasionally brown, spots are revealed on irradiation under UV light. For a more detailed description of the TLC procedures, see ref. 13.

GLC of Halowax 1014 and 1051 was carried out on a Pye 104 chromatograph

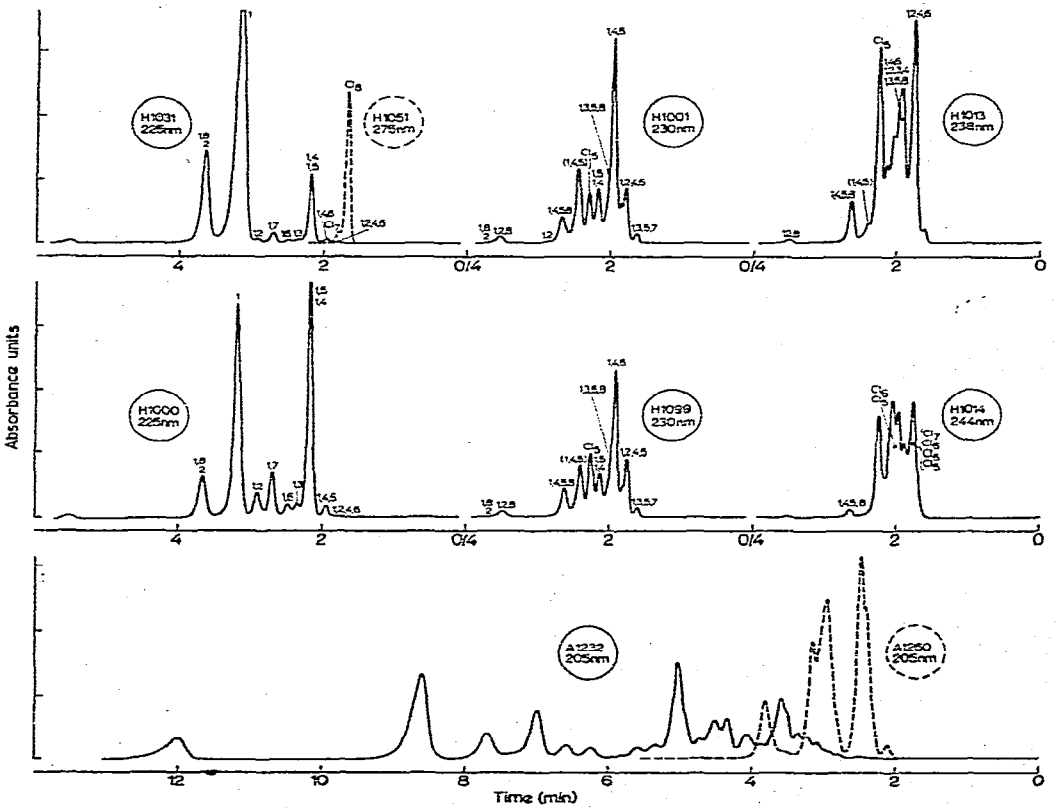

Fig. 1. HPLC of Halowax 1031, 1000, 1001, 1099, 1013, 1014 and 1051 (*ca.* 300 ppm in *n*-hexane). Conditions: column, 25 cm × 3 mm I.D. filled with 5-μm LiChrosorb SI 60; mobile phase, dry *n*-hexane; flow-rate, 1.4 ml·min^{-1}; UV detection at the wavelengths indicated; full scale, 1.28 (Halowax 1031, 1000, 1001 and 1099), 0.64 (Halowax 1013 and 1014), 2.56 (Halowax 1051) absorbance units; temperature, 27 ± 1°. Tentative assignments are indicated by parentheses. For reference, chromatograms of Aroclor 1232 and 1260[5] have been included.

equipped with a ^{63}Ni electron-capture detector, at 220 and 260°, respectively, with 4% OV-101 on Chromosorb W HP, 80–100 mesh, as the stationary phase.

UV spectra were recorded on a Beckman Acta CIII spectrometer using cells with quartz windows.

RESULTS AND DISCUSSION

HPLC and UV spectrometry of the Halowaxes

HPLC chromatograms of seven commercially available PCN mixtures (Halowax 1031, 1000, 1001, 1099, 1013, 1014 and 1051) are presented in Fig. 1; they were recorded at or near their wavelength of maximum absorption, as indicated in the figure. HPLC chromatograms of two PCB mixtures (Aroclor 1232 and 1260) are included in order to facilitate comparisons. The results show clearly that the chromatograms of each of the Halowaxes have a characteristic pattern and range of retention times; the similarity between the chromatograms of Halowax 1001 and 1099 is to be expected on the basis of their nearly identical chlorine contents. A detailed discussion of this behaviour, which parallels that of the substituted biphenyls[2] and terphenyls[14], is presented below. The chromatograms of the Halowaxes display a smaller number of peaks than the PCB mixtures, because of the smaller number of PCN isomers possible (75 compared with 209 for the PCBs) and the relatively short elution time range of the PCNs (*ca.* 4 min) compared with the PCBs (*ca.* 10 min).

Comparison of the chromatograms recorded for the Halowaxes and the Aroclors in Fig. 1 and ref. 2 reveals that the major peaks of the low-chlorinated Aroclors (1221–1242) will be eluted separately from those of all Halowaxes. However, with increasing chlorine content of the Aroclors, their retention time ranges decrease and serious overlap with the peaks of the Halowaxes begins to occur. With Aroclor 1260 and 1268, no useful separation is possible. As a further complication, one should bear in mind that an appreciable number of common pesticides[2] and polychlorinated terphenyls[14] are also eluted in the retention time range characteristic of PCNs and PCBs. However, HPLC can effectively be used for the simultaneous identification of PCNs and, *e.g.*, PCBs, either by using multi-wavelength detection or by the introduction of a per- or dechlorination step (see above) prior to chromatography. The former aspects will be briefly discussed.

All of the UV spectra of the PCBs display a strong absorption band in the 195–215-nm range ($\log \varepsilon = 4.6$–5.1) and a much weaker, often rather flat, band around 240 nm ($\log \varepsilon < 4.3$). A very weak band ($\log \varepsilon = 2.5$) between 265 and 305 nm is observed with highly *ortho*-substituted biphenyls only. As for the Halowaxes, the data in Table I and Fig. 2 show that their main absorption band shifts to the red end of the spectrum with increasing chlorine content and falls in the region 224–244 nm for all products except Halowax 1051, which has $\lambda_{max.} = 275$ nm; $\log \varepsilon$ values are between 4.7 and 4.8, except for Halowax 1031, for which $\log \varepsilon_{224} \approx 5.0$. More-important, the Halowaxes also display a series of absorption maxima between 275 and 320 nm; $\log \varepsilon$ values are between 3.7 and 4.1. As a consequence, detection at two different wavelengths, lying in the 195–215- and 275–320-nm region, respectively, will help to discriminate between PCBs and PCNs. Fig. 3 summarizes the results of the analysis of mixtures of equal amounts of a Halowax and an Aroclor; a third wavelength, 254 nm, has been included as it is the wavelength commonly used in photom-

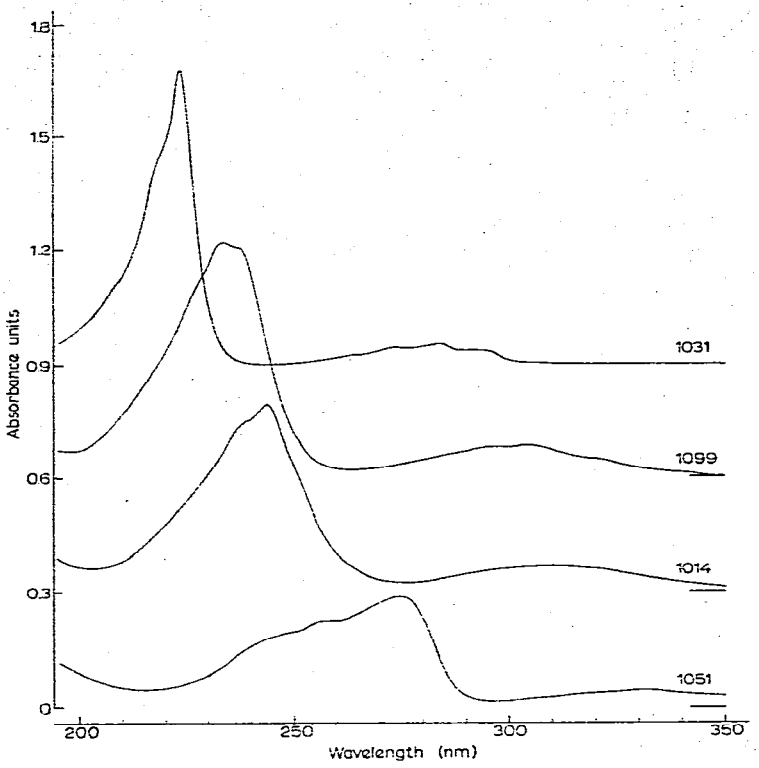

Fig. 2. UV absorption spectra of Halowax 1031, 1099, 1014 and 1051. Concentration, 20 ppm of Halowax in *n*-hexane; cell pathlength, 1 mm (Halowax 1031) or 2 mm (Halowax 1099, 1014 and 1051).

etric detectors in liquid chromatography. From Fig. 3 and similar data obtained for other PCN–PCB mixtures, one can draw the following conclusions: (a) if an appreciable amount of a Halowax is present next to an Aroclor, the characteristic HPLC pattern of the latter is drastically changed even at 205 nm, thus making identification of PCBs more complicated; (b) absorption measurements carried out at 254 nm yield results that are inferior to those obtained at either 205 or 305 nm; (c) absorption measurement at 305 nm can be recommended for the identification of Halowaxes, if PCBs are thought to be present. Admittedly, detection of the Halowaxes in the 275–320-nm region instead of at their wavelength of maximum absorption causes an approximately 10-fold decrease in sensitivity, *i.e.*, the detection limit increases to 10–20 ppm in hexane.

HPLC and UV spectrometry of individual PCNs

In order to study more closely the dependence of the retention times and the UV spectral behaviour of the constituents of the Halowaxes on their chlorine content, HPLC was carried out on 33 individual PCNs and naphthalene, and UV spectra were recorded in the 200–360-nm region. In all but two instances, HPLC showed the PCNs to have a purity of *ca.* 98% or more; a sample of 1,2-dichloronaphthalene was found to contain mainly 1,3- and 2,3-dichloronaphthalene, plus di- or trichloronaph-

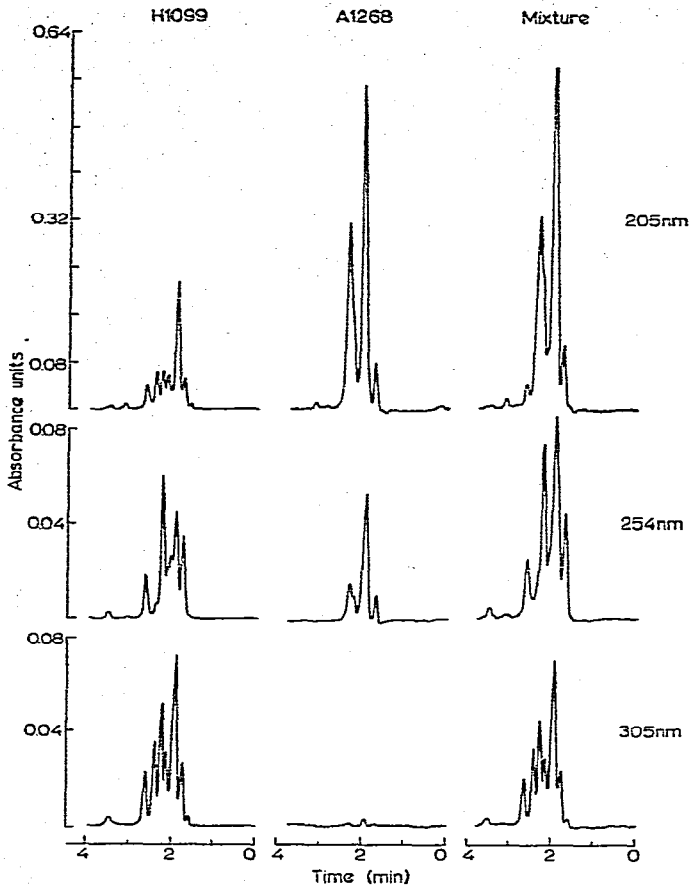

Fig. 3. UV detection at 205, 254 and 305 nm in the HPLC of Halowax 1099, Aroclor 1268 and their 1:1 mixture. Concentrations: *ca.* 200 ppm of Halowax and Aroclor each, dissolved in *n*-hexane. Other conditions as in Fig. 1.

thalene, and was therefore rejected. The relevant chromatographic and spectral data are summarized in Table II; several spectra are shown in Fig. 4. As only minute amounts of material were available for most of the samples, no data on molecular extinction coefficients are included in the table.

HPLC. The HPLC results demonstrate that, in general, the introduction of an increasing number of chlorine atoms into a particular PCN leads to a decrease in retention time, as shown by series such as:

0 > 1- > 1,2- > 1,2,3- > 1,2,3,5- > 1,2,3,5,7-
0 > 1- > 1,4- > 1,4,6- > 1,2,4,6-
0 > 2- > 2,3- > 2,3,6- > 1,2,3,7-

where "0" represents naphthalene. However, no strict relationship exists, the retention varying widely with both the number and position of the chlorine atoms in the naphthalene nucleus (*cf.* ref. 2). For example, substitution in (non-adjacent) α-positions appears to decrease the retention to a greater extent than does (non-adjacent) β-sub-

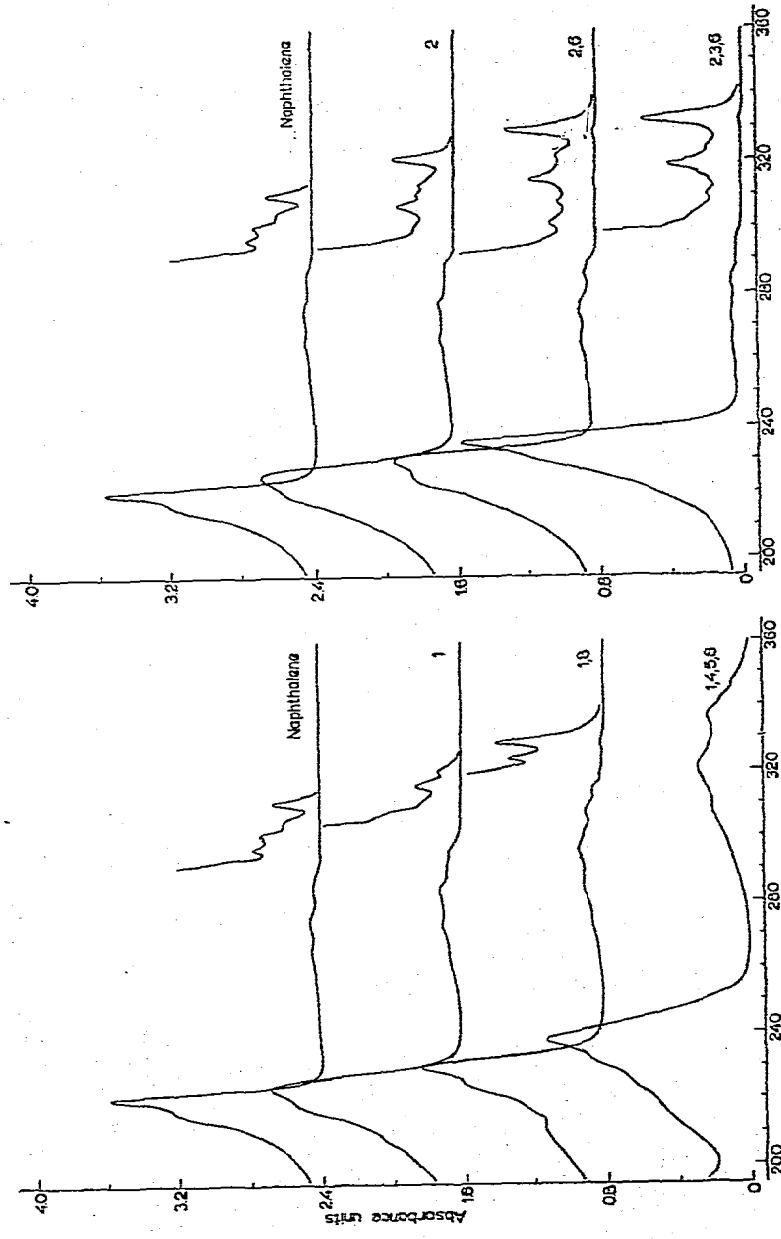

Fig. 4. UV absorption spectra of naphthalene (10 ppm) and 1-mono-, 1,8-di-, 1,4,5,8-tetra-, 2-mono-, 2,6-di- and 2,3,6-trichloronaphthalene (*ca.* 25 ppm in *n*-hexane). Cell pathlength, 2 mm. L_b band, × 60.

TABLE II

HPLC RETENTION TIMES AND UV SPECTRAL DATA FOR 33 PCNs AND NAPHTHALENE

HPLC conditions: silica gel (5 μm LiChrosorb SI 60)/dry *n*-hexane; flow-rate, 1.4 ml·min^{-1}; UV detection at $\lambda_{max.}$; temperature, 27 ± 1°. UV conditions: solutions of PCNs in *n*-hexane; Beckman Acta CIII spectrometer.

No.	*Substituted PCN*	t_R *(min)*	$\lambda_{max.}$ *(nm)* *	
			B_b band	*L_a band*
0	Naphthalene	5.40	218s, 221	257, 265, 274, 285
1	1-	3.15	219s, 223	264, 273, 284, 295
2	2-	3.60	221s, 225	257, 267, 277, 288
3	1,2-	2.90	215s, 218s, 224s, 230	267, 275, 285, 297
4	1,3-	2.30	214s, 225s, 229	267, 276, 286, 297
5	1,4-	2.15	213s, 224	272, 281, 292, 309
6	1,5-	2.15	217s, 223s, 227	272, 281, 292, 309
7	1,6-	2.45		
8	1,7-	2.65		
9	1,8-	3.65	217s, 220s, 226s, 230	274, 285, 295, 307
10	2,3-	3.30	216s, 220s, 225s, 230	263, 272, 283, 294
11	2,6-	2.80	215s, 219s, 226s, 230	259, 268, 277, 288
12	2,7-	2.80	216s, 221s, 228s, 231	262, 270, 280, 290
13	1,2,3-	2.55	217s, 230s, 234	268, 278, 289, 300
14	1,2,5-	2.00	216s, 221s, 228s, 233	272, 282, 293, 304
15	1,2,6-	2.35	217s, 230s, 234	264, 274, 284, 296
16	1,2,7-	2.60	220s, 223s, 229s, 234	268, 278, 289, 302
17	1,2,8-	3.50	218s, 231s, 235	275, 287, 298, 310
18	1,3,6-	2.00	219s, 230s, 234	268. 279, 290, 302
19	1,3,7-	2.15	217s, 222s, 229s, 234	260, 274, 284, 296
20	1,3,8-	2.70	217s, 222s, 230s, 235	275, 287, 298, 311
21	1,4,6-	1.95	217s, 222s, 227s, 233	275. 285, 296, 309
22	2,3,6-	2.75	220s, 230s, 235	263, 273*, 284, 295
23	1,2,3,4-	1.95	227s, 232, 238	274, 285, 296, 309
24	1,2,3,5-	1.90	240	276, 287, 298, 311
25	1,2,3,7-	2.35	227s, 237, 240	270, 280, 290, 303
26	1,2,4,6-	1.75	221s, 235s, 237	275, {286, 291* {298, 303 310
27	1,3,5,7	1.60	220s, 227s, 233, 239	279, {287, 291* {300, 303 311
28	1,3,5,8-	2.00	221s, 238	285, 297, 308, 321
29	1,3,6,7-	2.05	223s, 233s, 239	{268, 273 {280, 284 {291, 296 303
30	1,4,5,8-	2.60	223s, 234s, 238	294, 307, 321, 336
31	1,4,6,7-	1.90	223s, 228s, 241s, 245	280, 290, 302, 314
32	1,2,3,5,7-	1.65	220s, 226s, 238s 244	{272, 279 {284, 290 {296, 301 {309, 314
33	1,2,3,4,5,6,7,8-	1.65	240s, 260s, 268s, 275	310, 322, 332, 345

* In the B_b band, the principal maximum is invariably found at the high-wavelength side; in the L_a band, the third and occasionally the second, $\lambda_{max.}$ recorded has the highest intensity.

stitution: 1-monochloronaphthalene moves ahead of the 2-isomer, 1,4- and 1,5-dichloronaphthalene are less retarded than are 2,6- and 2,7-dichloronaphthalene and 1,4,6-trichloronaphthalene has a lower retention time than has the 1,3,7-isomer.

A different picture emerges if substitution occurs in adjacent positions. This

TABLE III

DEPENDENCE OF RETENTION TIMES OF DI- AND TETRASUBSTITUTED PCNs ON THE POSITION OF THEIR CHLORINE ATOMS

HPLC system: see Table II.

Di-PCN	t_R *(min)*	*Position of adjacent Cl atoms*	*No. of α-Cl atoms*	*Tetra-PCN*	t_R *(min)*	*Position of adjacent Cl atoms*	*No. of α-Cl atoms*
1,4-	2.15	—	2	1,3,5,7-	1.60	—	2
1,5-	2.15	—	2	1,2,4,6-	1.75	1,2-	2
1,3-	2.30	—	1	1,4,6,7-	1.90	2,3-	2
1,6-	2.45	—	1	1,2,3,5-	1.90	1,2; 2,3-	2
1,7-	2.65	—	1	1,2,3,4-	1.95	1,2; 2,3-	2
2,6-	2.80	—	0	1,3,5,8-	2.00	1,8-	3
2,7-	2.80	—	0	1,3,6,7-	2.05	2,3-	1
1,2-	2.90	1,2-	1	1,2,3,7-	2.35	1,2; 2,3-	1
2,3-	3.30	2,3-	0	1,4,5,8-	2.60	1,8-	4
1,8-	3.65	1,8-	2			1,8-	

causes an increase in retention time, especially when chlorine atoms are introduced into a PCN in such a way that 1,8-substitution results. To quote some examples: 1,8-dichloronaphthalene not only has a much higher retention time than have the 1,4- and 1,5-isomers, but its retention also surpasses that of 1-monochloronaphthalene, while 1,2,8- and 1,3,8-trichloronaphthalene are retained more strongly than are 1,2- and 1,3-dichloronaphthalene, respectively. Further, one should note that 1,4- and 1,5-dichloronaphthalene move ahead of 1,4,5,8-tetrachloronaphthalene, despite the two additional chlorine atoms present in the nucleus of the latter compound. The presence of chlorine atoms in the 2,3-position also promotes retention, although to a lesser extent than with 1,8-substitution. This effect is demonstrated by the fact that 2,3-dichloronaphthalene has a higher retention time than all other disubstituted PCNs, except 1,8-dichloronaphthalene, and that all trisubstituted PCNs studied, except 1,2,8-trichloronaphthalene, move ahead of 2,3,6-trichloronaphthalene. An illustrative summary of the above rules for the di- and tetrasubstituted PCNs is shown in Table III. Lastly, in all probability, the complete absence of substitution in any adjacent position causes 1,3,5,7-tetrachloronaphthalene to move ahead of all PCNs studied, including octachloronaphthalene.

UV spectra. The spectra of the PCNs were recorded chiefly with a view to selecting the proper wavelength during detection in HPLC. However, their diagnostic value justifies further discussion, especially as only a limited number of data on the spectra of polychlorinated and other polysubstituted naphthalenes have been published. Such a discussion will turn on the fact that the aromatic hydrocarbons generally display three $\pi \rightarrow \pi^*$ absorption bands in the accessible ultraviolet region[15,16]*. The L_a bands, which have an intensity of about $\log \varepsilon = 4$, are correlated with a localization of two π-electrons in *p*-positions. The L_b bands, which are sometimes hidden behind the L_a bands, *e.g.*, with asymmetrically arranged ring systems, have intensities that

* The notations L_a, L_b and B_b are used instead of *p*, α and β, respectively, in order to prevent confusion with the terms α- and β-substitution.

are usually in the range log ε = 2–3. The B_b bands are the most intense (log ε = 4–6) in the spectrum of an aromatic hydrocarbon, and are never obscured by other transitions.

Naphthalene indeed has three main bands in the accessible ultraviolet region. The B_b band displays maximum absorption at 221 nm (log ε = 5.0–5.1) with a prominent shoulder at 218 nm; the L_a band has its main maxima at 265 and 274 nm (log ε = 3.6–3.8), and the relatively weak and therefore less interesting L_b band (log ε = 2.3–2.5) is observed in the 290–315-nm range (Fig. 4)[15]. Introduction of chlorine atoms into the naphthalene nucleus induces a shift of the B_b band towards the visible region. The magnitude of this shift is chiefly determined by the number of substituents and is largely unaffected by their position, as is clearly evident from the following summary: mono-, 223–225 nm; di-, 224–231 nm; tri-, 233–235 nm; tetra-, 238–245 nm. Although accurate values of the molar extinction coefficients for individual PCNs could not be determined, the data for the Halowaxes quoted above allow one to conclude that the B_b bands of di- and higher substituted PCNs generally are distinctly less intense than is the B_b band of naphthalene.

Changes in the L_a and L_b bands are more complicated than are those in the B_b band, being determined by both the number and position of the chlorine atoms in the naphthalene nucleus. The effect of extending conjugation in a given direction by substitution will primarily affect a band polarized in that direction. Thus, α-substitution should cause bathochromic and hyperchromic effects predominantly in the transverse-polarized L_a band, while β-substitution should extend conjugation primarily in the longitudinal direction and thus cause mainly a red shift and intensify the longitudinally polarized L_b band. (However, one must bear in mind that with increasing substitution steric hindrance, which may be expected[17] to produce a hypsochromic displacement, will counteract the normal red shift.) These predictions are confirmed by comparing, *e.g.*, the data for 1- and 2-monochloronaphthalene, or even better, those for 1,4-, 1,5- and 1,8- with those for 2,3-, 2,6- and 2,7-dichloronaphthalene. Without exception, substitution in the α-position(s) leads to a marked red shift of the L_a band, *viz.*, over a distance of *ca.* 10 and 20 nm for mono- and disubstituted PCNs, respectively. The effect of α-substitution is still more pronounced with 1,4,5,8-tetrachloronaphthalene; here, the L_b band is completely hidden under the L_a band, which has shifted far towards the red end of the spectrum. With the β-substituted PCNs, on the other hand, the position of the L_a band hardly changes. Instead, an intensification of the L_b band is observed. However, contrary to statements made in the literature[16], the bathochromic shift of the L_b band is about equal for α- and β-substituted naphthalenes: its high-wavelength maximum occurs at 321 and 322 nm for 1- and 2-monochloronaphthalene, respectively, and at 324–329 and 325–330 nm for the di-α- and di-β-substituted isomers, respectively. Lastly, the large difference between the wavelengths of maximum absorption of the L_a band observed for 1,3,5,8- and 1,2,3, 7-tetrachloronaphthalene is in complete agreement with the above conclusions.

Our results are in good agreement with literature data for, *e.g.*, mono- and/or dimethyl-, bromo- and aminonaphthalenes[16,18]. In particular, comparison of the UV absorption spectra of the PCNs with those publishd by various workers[16–18] for polymethylnaphthalenes (*cf.*, Table IV) reveals a striking similarity. As for the intensity of the L_b band, one should bear in mind that increasing α-substitution, which induces an overlap of the L_a and L_b bands, will cause an increase in the molar extinction co-

TABLE IV

LITERATURE DATA ON PRINCIPAL UV MAXIMA OF POLYMETHYLNAPHTHALENES (PMN)

PMN	$\lambda_{max.}$ *(log ε)*						*Ref.*
	B_b band	*L_a band*			*L_b band*		
1-	224 (4.8)	271	281 (3.8)	291	312	317 (2.2)	18
2-	224 (4.9)	265	275 (3.7)	285	312	319 (2.7)	18
1,4-	—	—	289 (3.9)	—	—	—	17
1,5-	228 (5.1)	276	287 (4.0)	298	317	321 (2.5)	16
1,8-	—	—	285 (3.9)	—	—	—	17
2,3-	—	—	279 (3.7)	—	—	—	17
2,6-	227 (5.1)	265	274 (3.7)	285	317	324 (3.0)	16
2,7-	—	—	275 (3.7)	—	—	—	17
1,4,5-	230 (4.9)	278	292 (3.9)	303	320	326 (3.0)	19
1,3,6-	230 (4.9)	276	284 (3.7)	293	313	320 (2.5)	19
1,4,5,8-	233 (4.8)	290	296 (3.9)	307	—	334 (3.3)	17
2,3,6,7-	229 (4.1)	260	270 (3.7)	280	—	325 (2.9)	17

efficients of the maxima of the L_b band of the α-substituted compared with the β-substituted tri- and tetramethylnaphthalenes, thus reversing the initial, normal sequence.

Composition of the Halowaxes

A preliminary study was made of the composition of the Halowaxes. Peaks were assigned by combining literature data on the GLC of the Halowaxes, particularly those of Beland and Geer[1], and the several results collected in Fig. 1 and Table II. It should be noted that all of the chromatograms in Fig. 1 were obtained at a flow-rate of the mobile phase of *ca.* 1.4 ml·min^{-1} (pressure 80 bar) and at a wavelength near to that of maximum absorption of the Halowax studied, whereas in practice many additional chromatograms have been run at lower pressures and/or different wavelengths, in order to increase the resolution and selectivity of the present chromatographic system.

The HPLC of Halowaxes 1031 and 1000 revealed the presence of 10–12 peaks (at 80 bar), all of which can be assigned to individual PCNs mentioned in Table II. With Halowax 1031, three large peaks occurred, attributable to both mono- and three dichloronaphthalenes. By selecting two appropriate wavelengths of detection, *viz.*, 225 and 230 nm (*cf.*, Table II), one can establish that the peak at $t_R = 3.60$ min is predominantly due to 2-monochloronaphthalene. As the UV spectral behaviour of 1,4- and 1,5-dichloronaphthalene is almost identical, no such conclusion can be reached concerning the peak at $t_R = 2.15$ min. Semi-quantitative analysis of Halowax 1031 was performed by peak area measurement at several wavelengths between 220 and 230 nm, *i.e.*, in the region of $\lambda_{max.}$ for naphthalene, and mono- and disubstituted PCNs, and averaging of the results so obtained in order to calculate weight percentages: naphthalene, $< 1\%$; 1-monochloronaphthalene, 75%; 2-monochloronaphthalene, 15%; (1,4- + 1,5-)-dichloronaphthalene, 8%; other PCNs, 2%. This result agrees well with the specifications of the manufacturer (92–96% of monochloronaphthalenes)[10]. The slight discrepancy cannot be attributed to preferential loss of the monochloronaphthalenes (and naphthalene) by evaporation, as the results proved to be independent of the age of the sample solution.

As for Halowax 1000, a shift from mono- to di- (and tri-) substituted PCNs can be seen, although 1-monochloronaphthalene is still one of the major constituents. Multiple detection at 225 and 230 nm (see above) clearly reveals that with Halowax 1000, 1,8-dichloronaphthalene contributes considerably to the peak with $t_R = 3.60$ min.

Halowaxes 1001 and 1099 are mixtures of about equal proportions (40%) of tri- and tetrachloronaphthalenes, and about 10% each of di- and pentasubstituted isomers[10]. From the pertinent chromatograms in Fig. 1 it can be seen that disubstituted PCNs are almost absent. Mass spectrometry showed the peak at $t_R = 2.30$ min to be attributed to a pentasubstituted PCN. As its UV absorbance in the region 320–360 nm increases relative to those of all other peaks present, it can be concluded that this PCN is the fully α-substituted 1,2,4,5,8-isomer. To quote another example of a conclusion reached by multiple-wavelength detection: at 230 nm, 1,3,5,8-tetrachloronaphthalene is barely visible as a shoulder on the prominent 1,4,6-trichloronaphthalene peak (Fig. 1), whereas it can clearly be distinguished when detection is effected at 245 nm. Lastly, samples of 1,2,4-, 1,3,5- and 1,4,5-trichloronaphthalene, all of which show prominent peaks in the gas chromatograms published by Beland and Geer[1], unfortunately were not available. However, on the basis of the rules concerning the dependence of the retention of PCNs on their structure outlined above, we tentatively suggest that the peak at $t_R = 2.40$ min is due to the tri-α-substituted 1,4,5-isomer.

No GLC analyses comparable with those of Beland and Geer[1] for the lower chlorinated PCN mixtures are known for Halowaxes 1013 and 1014. However, taking into account that the most common substitution patterns for tri- and tetrasubstituted PCNs can be read from the results obtained for Halowaxes 1001 and 1099, a considerable number of tentative assignments can confidently be made for the next higher chlorinated PCN mixture, *i.e.*, Halowax 1013 (see Fig. 1). It may be added that the peak at $t_R = 2.30$ min shows the same UV behaviour as the corresponding peak in Halowaxes 1001 and 1099. With Halowax 1014, several of its main peaks were separately collected and analyzed by GLC, and the results interpreted on the basis of data published by Goerlitz and Law[4]. Preliminary conclusions are included in Fig. 1. The hepta- and the two hexasubstituted isomers constitute 40–50% of Halowax 1014, whereas they are virtually absent from Halowax 1013[4,10].

For the analysis of Halowax 1051, see the section *TLC of Halowaxes*.

Lastly, it is worth mentioning that HPLC has been applied to the analysis of a sample of "technical dichloronaphthalene" (Eastman Kodak, Rochester, N.Y., U.S.A.). The sample was found to consist of about 45% of 1-monochloronaphthalene and 25% of (1,4- + 1,5-)-dichloronaphthalene. In addition, small amounts of naphthalene, 2-monochloronaphthalene, many, if not all, other disubstituted isomers, and some unknown higher chlorinated PCNs are present. Actually, comparison of the HPLC chromatogram of technical dichloronaphthalene with those presented in Fig. 1 indicates its composition to be intermediate between those of Halowax 1031 and 1000.

Composition of Nibren and Clonacire mixtures

Nibren D88 and Clonacire 90 display HPLC chromatograms that are virtually identical with those of Halowax 1001. This conclusion is corroborated by their similar UV spectra and melting points (Table I). The more highly chlorinated Nibren D116N

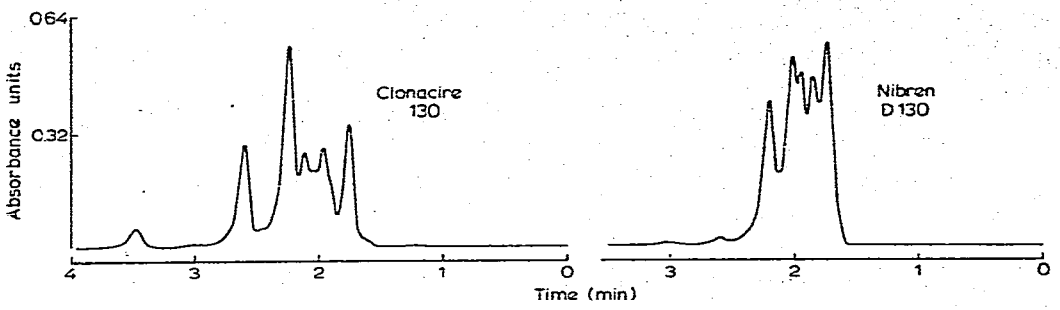

Fig. 5. HPLC of Clonacire 130 and Nibren D130 (*ca.* 200 ppm in *n*-hexane) recorded at 244 nm. Conditions as in Fig. 1.

and Clonacire 115 strongly resemble Halowax 1013 in their HPLC chromatograms and melting points. In the chromatograms, one of the most prominent, although still small, differences concerns the relative heights of the three central peaks. Whereas the peak at $t_R = 1.80$ min is the most prominent in Halowax 1013, the peaks at $t_R = 2.00$ and 2.30 min are the main peaks in Clonacire 115 and Nibren D116N, respectively. Moreover, Halowax 1013 contains a smaller proportion of 1,4,5,8-tetrachloronaphthalene than do the other two mixtures.

The HPLC chromatograms of Nibren D130 and Clonacire 130 are distinctly different from each other (Fig. 5). Except for relatively minor differences, the chromatogram of Nibren D130 resembles that of Halowax 1014. As for Clonacire 130, its melting point and UV spectrum suggest the mixture to have a chlorine content intermediate between those of Halowax 1013 and 1014. This conclusion appears to be confirmed by HPLC: compared with Halowax 1014, Clonacire 130 contains relatively large proportions of 1,2,8-tri-, 1,3,5,7-tetra- and 1,4,5,8-tetrachloronaphthalene.

Summarizing the above discussion, we can state that for five of the six mixtures investigated, their main constituents can be read from the assignments made for the corresponding Halowaxes (Fig. 1).

TLC of Halowaxes

TLC was carried out in systems previously used by us for the analysis of PCB mixtures[13], *viz.*, silica gel/*n*-hexane and Kieselguhr impregnated with paraffin oil/acetonitrile–methanol–water (8:9:3). Results for six Halowaxes are presented in Fig. 6. Chromatograms for Halowax 1031 are not included, as they display a few vague zones at best: most of the constituents of this low-boiling PCN mixture evaporate during development. As for the other Halowaxes, the number of zones may vary slightly from one series of chromatograms to another, especially with the reversed-phase systems (detection of weak zones; overlapping of nearly contiguous bands). However, this does not seriously detract from the potentiality of TLC as a technique for discriminating between the various PCN mixtures. The separations obtained with reversed-phase TLC are superior to those for the system silica gel/*n*-hexane: with the former technique, about twice as many spots are observed (Fig. 6a and 6b). The resolution of the more highly chlorinated Halowaxes can be improved still further by using acetonitrile–methanol–acetone–water (20:20:9:1) as the mobile phase. Three examples are shown in Fig. 6c. The results compare favourably with those

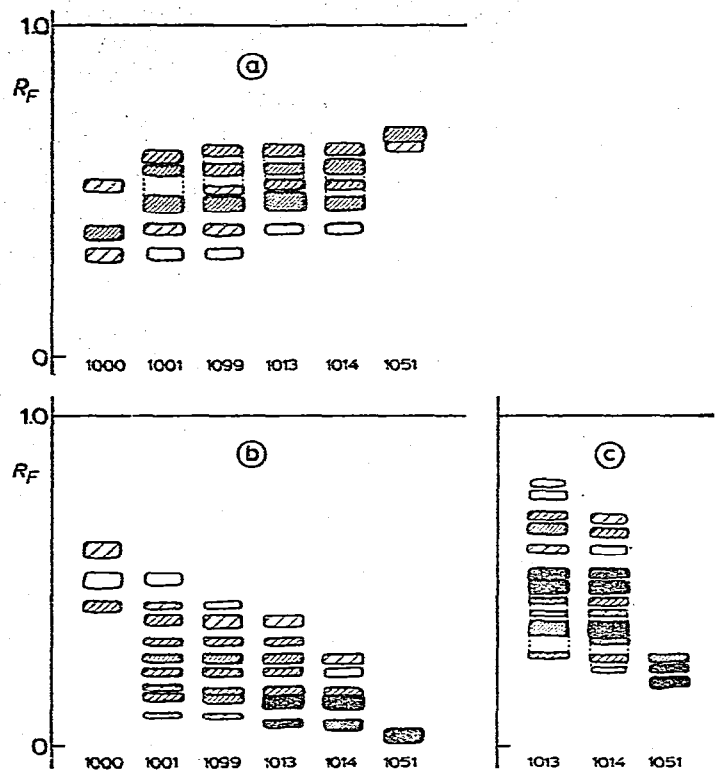

Fig. 6. TLC of Halowax 1000, 1001, 1099, 1013, 1014 and 1051 in three systems: (a) silica gel/*n*-hexane; (b) Kieselguhr impregnated with paraffin oil/acetonitrile–methanol–water (8:9:3); (c) Kieselguhr impregnated with paraffin oil/acetonitrile–methanol–acetone–water (20:20:9:1). Conditions, see text.

of Stalling and Huckins[3], who reported the presence of 5–7 spots in the reversed-phase TLC of Halowax 1099, 1013 and 1014.

The results obtained with Halowax 1051 merit special attention. Three well separated zones are observed on the chromatogram shown in Fig. 6c, whereas only two peaks occur in HPLC (Fig. 1) and GLC[3,5]. Elution of the pertinent zones from the thin layer, followed by analysis by GLC, HPLC and mass spectrometry, allows us to reach definite conclusions* concerning peak assignment for all three chromatographic techniques. These are summarized in Table V. It should be added that the analysis of Halowax 1051 by HPLC at relatively low pressure (10–20 bar) revealed the second heptasubstituted PCN as a shoulder on the peak due to octachloronaphthalene.

For Halowax 1014, the zones obtained by normal and reversed-phase TLC were scraped off the thin-layer plate, eluted with *n*-hexane, dried over a molecular sieve

* Using samples of the heptachloronaphthalenes provided by Dr. B. J. Wakefield[20], it has recently been shown by us that the peaks at t_R = 1.70 and 1.80 min can be attributed to the 1H- and 2H-hepta-isomer, respectively. This is according to expectations: the faster moving 1H-isomer has only one pair of Cl atoms in the 1,8-position, whereas with the 2H-isomer all four α-positions are occupied by Cl atoms.

TABLE V

CHARACTERISTICS OF HEPTA- AND OCTACHLORONAPHTHALENES

Substituted PCN	*R_F in reversed-phase TLC*	*$t_{rel.}$ in GLC*	*t_R in HPLC (min)*
Hepta-	0.27	0.63	1.80
Hepta-	0.23	0.63	1.70
Octa-	0.19	1.00	1.65

and analyzed by HPLC. The result is recorded in Fig. 7. As the chromatographic systems used in normal TLC and HPLC are the same, the similarity of the pertinent chromatograms is not surprising. As for reversed-phase TLC, a qualitative "reversal" of the peak sequence of the PCN mixture occurred, the lower chlorinated PCNs generally displaying higher R_F values. However, within neither of the prominent R_F/t_R ranges indicated in the lower half of the figure does a strict relationship between R_F and t_R appear to exist. This is contrary to our earlier observations on the HPLC and reversed-phase TLC of PCB mixtures[13], where such a strict relationship was found to apply for Aroclor 1254 and 1260.

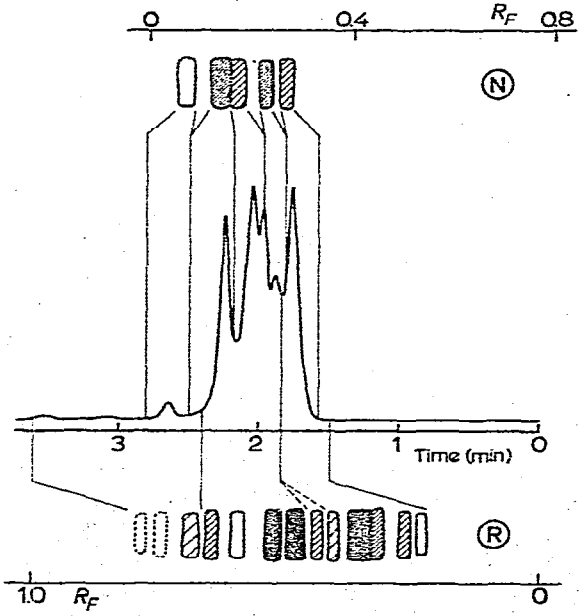

Fig. 7. Comparison of the behaviour of Halowax 1014 in HPLC and in normal (N) and reversed-phase (R) TLC. For details, see Figs. 1, 6a and 6c.

CONCLUSIONS

The results presented above enable us to reach several conclusions, as follows.

(1) HPLC in the system silica gel–dry *n*-hexane allows a rapid qualitative and semi-quantitative analysis of PCN mixtures. Comparison of literature data on GLC

with the present HPLC results shows a very satisfactory overall agreement. For the remainder, gas chromatographic analysis yields a better resolution: 25–30 separate peaks occur compared with 10–12 in HPLC. On the other hand, to quote Beland and Geer[1], the electron-capture chromatograms are misleading as to the amount of each isomer present, as the detector response shows its largest increase in the mono- to trichloro range. In other words, HPLC coupled with UV detection is the preferred technique if rapid information on the approximate composition of a PCN mixture is desired. Multiple-wavelength detection will add considerably to the potentialities of this method of analysis.

(2) TLC is a rapid, although relatively insensitive, technique for the qualitative analysis of PCN mixtures, reversed-phase TLC being superior to the normal technique. The favourable comparison of the number of spots obtained in reversed-phase TLC with the number of peaks apparent in normal HPLC for, *e.g.* Halowax 1014 and 1051, suggests that the analysis of PCN mixtures by reversed-phase HPLC will yield excellent resolution.

(3) The retention behaviour of individual PCNs in HPLC appears to be determined by two main effects: (a) increasing introduction of chlorine atoms in the naphthalene nucleus decreases retention, non-adjacent α-substitution surpassing non-adjacent β-substitution in this respect; (b) substitution in the 1,8- and, although less so, in the 2,3-positions, considerably promotes retention.

(4) In the UV spectra, the position of the B_b band is chiefly determined by the number of chlorine atoms present in the PCN. As for the position of the chlorine atoms, α-substitution causes a distinct bathochromic shift of the L_a band; the effect of β-substitution, *i.e.*, an intensification of the L_b band, is often obscured owing to the partial overlap of the L_b by the L_a band.

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