Journal of Chromatography, 127 (1976) 203–243
Chromatographic Reviews

CHREV. 97

POLYCHLORINATED NAPHTHALENES

U. A. Th. BRINKMAN and H. G. M. REYMER
Department of Analytical Chemistry, Free Reformed University, Amsterdam (The Netherlands)
(Received September 7th, 1976)

CONTENTS

I. INTRODUCTION

Laurent[1], in 1833, observed that wax-like materials result from the reaction of chlorine with naphthalene in the presence of certain catalysts. Almost 50 years later, these chlorination products were further studied by Fischer[2] and, shortly after 1900,

Aylsworth[3–5] patented the use of chlorinated naphthalenes for impregnating wood, paper, textiles and other materials. Chlorinated naphthalene waxes first became of importance during World War I as protective coating materials, particularly in Germany. In Germany, several firms took up the production of polychlorinated naphthalenes (PCNs), including Chemische Fabrik Griesheim Elektron, which used its so-called Perna waxes to impregnate paper inlays in gas-masks.

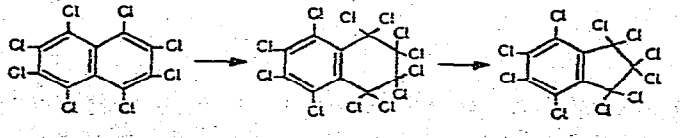
To-day, well known series of PCNs include the Halowaxes, Nibren waxes and Clonacires (see Section II.1), for which a variety of uses has been suggested related to their electrical, flame-retardant and fungus-resistant properties, stability and compatibility with other materials. The physical and chemical properties of PCNs and polychlorinated biphenyls (PCBs) are rather similar, and PCNs are manufactured for uses analogous to those of PCBs. As is now well known, PCBs are widespread and persistent industrial pollutants of the environment, and so are PCNs. Unfortunately, little information is available on the world-wide production of PCNs. According to one source[6], in 1956 the output of PCNs in the U.S.A. was about 3500 short tons, while the present total world market for PCNs has been estimated at "... probably less than 800 tons"[7]. The production of PCNs has also been claimed[8] to be at least 10% of that of PCBs, which has been estimated[9] at 33,000 and 13,000 metric tons for domestic sales of Monsanto's Aroclors only, in 1970 and 1972, respectively*.

Prior to this review, Fishbein[10] and Sherma[11] discussed the analysis of PCNs, and Kimbrough[12] wrote an extensive survey of toxicological aspects of PCNs and similar compounds. Much technical information can be derived from an early paper by Hardie[6] and from manufacturer's bulletins[13,14]. Recently, Kover[15] published a comprehensive environmental hazard assessment report on PCNs.

II. SYNTHESIS

1. PCN mixtures

Commercially available mixtures of PCNs are generally produced[6] by chlorinating naphthalene with chlorine gas in the presence of *ca.* 0.5 wt.-% of iron(III) or antimony(V) chloride. Chlorination is begun at 80° and the temperature is slowly increased as the reaction proceeds. During the process, the mixture is agitated continuously. When the desired pour-point has been reached, the chlorinated product is neutralized by stirring it in the molten state with aqueous alkali solution, washed with water and finally dried under vacuum. It should be noted that as chlorination proceeds, there is an increasing tendency towards the formation of products of simultaneous substitution and addition of chlorine. Thus, if chlorination is continued beyond the octachloronaphthalene stage, at temperatures above 200° in the presence of iron(III) chloride, four additional chlorine atoms can be readily introduced; simultaneously, liberation of carbon tetrachloride and transformation of the naphthalene ring system occur[16]:



(1)

Octachloronaphthalene Perchloroindane

* The large decrease in output after 1970 was due to voluntary restriction by Monsanto of sales of PCBs essentially to uses in closed systems.

Manufacturers of PCNs produce series of materials appropriate to the various uses to which the substances are to be put. In this section, the commercially available products are exemplified by reference to four such series.

(a) Halowaxes

Koppers Co. (Pittsburgh, Pa., U.S.A.) markets[13] a large series of light-coloured PCN mixtures under the trade-name Halowax. These products range from a liquid with a melting point of −33° to a mixture containing *ca.* 90% of octachloronaphthalene and melting at 185°. Information regarding the composition of the Halowaxes is presented in Table 1; their main physical and chemical properties are summarized in Table 2.

TABLE 1

APPROXIMATE COMPOSITIONS (WT.-%) OF HALOWAXES

Halowax	*Type of PCN*							
	Mono-	*Di-*	*Tri-*	*Tetra-*	*Penta-*	*Hexa-*	*Hepta-*	*Octa-*
1031	95	5						
1000	60	40						
1001		10	40	40	10			
1099		10	40	40	10			
1013			10	50	40			
1014				20	40	40		
1051							10	90

Halowaxes 2141 and 2148, not mentioned in these tables, are special-purpose blends for use in the electrical industry.

(b) Nibren waxes

These materials, produced[14] by Bayer (Leverkusen, G.F.R.) and formerly by I.G. Farbenindustrie, are crystalline solids with a chlorine content of *ca.* 50–60%; they are marketed as powders or flakes. Important physical characteristics of the vacuum-distilled Nibren D88, D116N and D130 waxes are recorded in Table 3.

Several further types of Nibren waxes have been reported[14,17], such as Nibren RN88 and RN130, and Nibren D130CM and D130CM/10. The RN-type products are dark-coloured non-vacuum-distilled analogues of Nibren D88 and D130. The other two products are modified PCN mixtures whose crystal structures oppose the penetration of water vapour very effectively.

(c) Seekay waxes

These waxes have been produced in Great Britain by ICI (Runcorn, Great Britain) and one of its forerunners since 1919. They are described[6] as wax-like solids with a light odour, and range in colour from pale yellow to black. Approximate melting points are from 67–73 to 120–125°. Two grades, produced in order to conform

TABLE 2

PHYSICAL AND CHEMICAL PROPERTIES OF HALOWAXES

Property	*Halowax*							
	1031	*1000*	*1001*	*1099*	*1099B*	*1013*	*1014*	*1051*
Physical form	liquid	liquid	flakes	flakes	flakes	flakes	flakes	powder
Cl content (approx. wt.-%C)	22	26	50	52	52	56	62	70
Specific gravity (at 25°C)	1.20	1.22	1.58	1.59	1.65	1.67	1.78	2.00
Initial boiling point at 760 mm Hg (°C)	250	250	308	315	322	328	344	310**
Approx. melting point (°C)	−25	−33	93	102	115	120	137	185
Flash point (°C, C.O.C.)	135	130	200	210	210	230	250	none to 430
Fire point (°C, C.O.C.)*	165	170	ntb	ntb	ntb	ntb	ntb	ntb
Max. acidity (mg KOH/g)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.1
Approx. viscosity (Saybolt univ. sec.)	35 (25°)	34 (25°)	30 (130°)	31 (130°)	31 (130°)	33 (130°)	35 (150°)	—
			Temperature (°C)					
			100	*100*	*115*	*130*	*150*	
Dielectric constant at 60 Hz	—	—	4.1	4.1	4.0	3.8	3.7	—
Dielectric constant at 1000 Hz	—	—	4.1	4.1	4.0	3.8	3.7	—
Power factor at 60 Hz	—	—	0.37	0.37	—	0.45	0.99	—
Power factor at 1000 Hz	—	—	0.005	0.005	0.01	0.04	0.44	—
Resistivity (MΩ·cm)	—	—	$1 \cdot 10^5$	$1 \cdot 10^5$	$1 \cdot 10^5$	$1 \cdot 10^5$	$1 \cdot 10^5$	—

* ntb = none to boiling.

** At 30 mm Hg.

TABLE 3

CHEMICAL AND PHYSICAL PROPERTIES OF NIBREN WAXES

Property	*Nibren*		
	D88	*D116N*	*D130*
Approx. melting point (°C)	90	113	135
Specific gravity (at 20 °C)	1.57	1.66	1.77
Shrinkage from 150° to 20 °C (%)	11	10	10
Viscosity (°*E*) at 150 °C	0.96	0.98	1.1
Acid number	0.01	0.02	0.03
Cl^- content (%)	$3 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
Dielectric constant at 800 Hz, 20 °C	5.0	4.7	4.5
Power factor (tg δ) at 800 Hz, 20 °C	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
Resistivity ($\Omega \cdot$cm) at 100 V, 1 min	$1 \cdot 10^{14}$	$1 \cdot 10^{14}$	$1 \cdot 10^{15}$
Disruptive strength ($kV \cdot cm^{-1}$)	150–200	150–200	200

to special electrical specifications, are known. Data[18] on the chlorine contents of the Seekay waxes, production of which was ceased about a decade ago, are summarized in Table 4.

(d) Clonacire waxes

Small amounts of three Clonacire waxes (90, 115 and 130) are produced by Prodelec (Paris, France). They differ in their degree of chlorination; the numbers correspond to the melting points.

Further information on the properties and uses of the PCN mixtures is presented below, while their spectral characteristics and behaviour in chromatography are discussed in the pertinent sections on analysis.

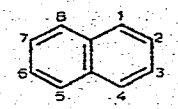
2. Individual PCNs

Theoretically, 75 different PCNs exist, as demonstrated in Fig. 1. However, on mechanistic and statistical grounds it is unlikely that all of them are formed in technical chlorination processes. More important, physically, the difficulty of isolating isomers from the mixtures produced by chlorination of naphthalene is such that indirect routes must be employed for all individual PCNs except 1-monochloro- and octachloronaphthalene. So far, the synthesis of 55 individual PCNs has been reported.

TABLE 4

CHLORINE CONTENTS OF SEEKAY WAXES

Grade	*Seekay wax*	*Cl content (%, w/w)*
R (refined or white wax)	68	46.5 ± 1
	93	50 ± 1
	123	56.5 ± 1
	700	43 ± 1
RC (electrical grades)	93	50 ± 1
	123	56.5 ± 1



No. of Cl atoms in one ring	No. of Cl atoms in other ring				
	0	1	2	3	4
0	N	2	4	2	1
1		6	12	8	2
2			13	12	4
3				6	2
4					1

Fig. 1. Naphthalene (N) and its chloro derivatives.

There is one main route according to which most PCNs are obtained in the laboratory. In order to synthesize, for example, a tetrasubstituted PCN, (one of) the corresponding trichloronaphthalenesulphonyl chloride(s) is heated for several hours with phosphorus(V) chloride at *ca.* 200°. The required sulphonyl chloride is often obtained by treating a suitable lower (tri-) substituted PCN with chlorosulphonic acid. Alternative routes include the use of a sulphonic acid instead of a sulphonyl chloride, and hydrolysis of a sulphonyl chloride with hydrochloric acid, in which event no additional chlorine atom is introduced into the naphthalene nucleus. As an illustration, a reaction scheme for the synthesis of several tetra- and one pentachloronaphthalene, taken from ref. 19 and simplified, is shown below.

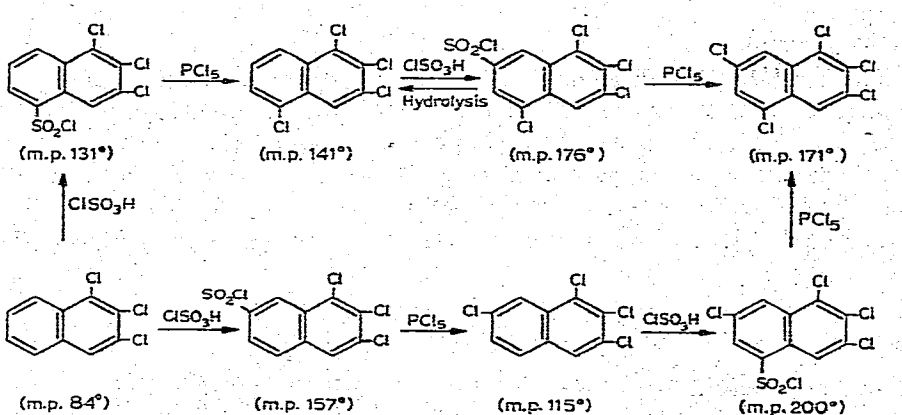


Table 5 records relevant characteristics of all PCNs that have been reported as pure products in the literature. Consultation of the papers by Wynne and co-workers[19,22,25,26,28–30,34] will usually suffice for those workers who are interested in PCNs synthesized from (poly)chloronaphthalenesulphonyl chlorides or -sulphonic acids. Therefore, further references have been omitted from Table 5. For all other compounds, details are listed in Table 6. Some further comments are given in the following sections.

TABLE 5

PHYSICAL PROPERTIES AND METHODS OF SYNTHESIS OF INDIVIDUAL PCNs

Methods of synthesis (see text): 1, $SO_2Cl_2 + PCl_5$; 2, sulphonic acid + Cl-containing reagent; 3, hydrolysis of sulphonyl chloride; 4, see Table 6.

PCN	*Melting point (°C)* *	*Boiling point (°C)*	*Density* (d_4^t)	n_D	*Dipole moment (D)* *	*Route*	
						No.	*Ref.*
1	−4 to −2.3	259.3^{760}	1.1938^{20}	1.6326^{20}	1.50–1.59	2	20
2	58–60	256	$1.1377^{70.7}$	$1.6079^{70.7}$	1.57–1.72	2	21
1,2	34–37	295–298	$1.3147^{48.5}$	$1.6338^{48.5}$	2.47	1	22
1,3	61.5–62	291^{775}			1.78	1	22
1,4	68–72	$286–287^{740}$	$1.2997^{75.9}$	$1.6228^{75.9}$	0–0.48	1	23
1,5	106.5–107	subl.			0	1	24
1,6	48.5–49	subl.			1.44	1	25
1,7	61.5–64	285–286	$1.2611^{99.5}$	$1.6092^{99.5}$	2.55	1	26
1,8	88–89.5	decomp.	$1.2924^{99.8}$	$1.6236^{99.8}$	2.82	3	27
2,3	119.5–120.5				2.55	3	28
2,6	135–141	285			0–0.60	1	23
2,7	114–116				1.53	1	29
1,2,3	81–84					4	19
1,2,4	92					3	28
1,2,5	74–79					1	19
1,2,6	90–92.5					1	29
1,2,7	88					1	29
1,2,8	83					2	27
1,3,5	102–103					1	28
1,3,6	80.5–81					1	19
1,3,7	112.5–113					1	30
1,3,8	89.5					1	30
1,4,5	130–131					1	19
1,4,6	65–68					1	28
1,6,7	109–109.5					1	28
2,3,6	90–91					1	19
1,2,3,4	196–198					4	19
1,2,3,5	141					1	19
1,2,3,7	115					1	19
1,2,4,6**	111					1	19, 31
1,2,4,7**	140–144					1	19, 32
1,2,5,6**	164					1	19, 33
1,2,5,7**	114					1	19, 31
1,2,6,8	125–127					4	34
1,3,5,7	178–181					1	19
1,3,5,8	131					1	19
1,3,6,7	119–120					1	19
1,4,5,8	183					4	35–37
1,4,6,7	139					1	19
2,3,6,7	135					4	38
1,2,8,*x*	135					1	19
1,4,5,*x* (*x*=3?)	144					1	19
2,3,6,*x*	218					1	19
x,*x*,*x*,*x*	176					4	38
1,2,3,4,5	168.5					4	39, 40

(Continued on p. 210)

TABLE 5 (*continued*)

PCN	Melting point (°C)*	Boiling point (°C)	Density (d_4^t)	n_D	Dipole moment (D)*	Route	
						No.	Ref.
1,2,3,4,6	147					1	19
1,2,3,5,7	171					1	19
1,2,3,5,*x*	177					4	37, 41
1,2,4,6,*x* ($x = 8$?)	135					1	19
1,3,5,8,*x*	155					1	19
1,3,5,8,*x*	—***					4	42
1,4,6,7,*x* ($x = 2$?)	131					1	19
1,2,3,4,5,6	—					4	43
1,2,4,5,6,8	175–177					4	38
1,2,3,4,5,6,7	—***					4	44
1,2,3,4,5,6,8	194					4	44, 45
1,2,3,4,-5,6,7,8	197.5–203					4	—

* Range of values found in the literature.
** See text for structure assignment.
*** Still impure.

(a) Mono-PCNs

Apart from the PCN mixtures, 1-monochloronaphthalene is the only chlorinated naphthalene that has so far proved to be of industrial utility. It is produced industrially by passing chlorine into molten naphthalene and fractionating the product. It can also be obtained in good yield[17,47,48] by chlorinating molten naphthalene in the presence of iodine, iron(III) chloride or antimony(V) chloride.

1- and 2-monochloronaphthalene can be prepared on a smaller scale from naphthalene-1-sulphonic acid on heating with copper(II) chloride[20] and from 2-monochloronaphthalene-1-sulphonic acid on treatment with dilute sulphuric acid[21].

(b) Di- and tri-PCNs

For some disubstituted PCNs, preparation from the sulphonyl chloride is not the preferred method. 1,3-Dichloronaphthalene, for instance, is obtained[49] in better yield by heating a solution of diazotised 2,4-dichloro-1-naphthylamine in dilute sulphuric acid with ethanol. With trisubstituted PCNs, both nitro and amino compounds have been used[19,27,28] as starting products instead of a sulphonyl chloride or sulphonic acid. For further details, the reader should consult compilations such as refs. 50 and 51.

(c) Tetra- and penta-PCNs

Turner and Wynne[19] were not able to elucidate the exact structures of several tetrasubstituted PCNs. According to Cencelj[31], 1,4,7,*x*-tetrachloronaphthalene (probably $x = 8$; ref. 19) is identical (melting point, IR spectrum) with the 1,2,4,6-tetrachloronaphthalene he synthesized himself. On the basis of melting point data, Cencelj also concluded that $x = 7$ in 1,2,5,*x*-tetrachloronaphthalene (m.p. 114°). Piggott and Slinger[33] have demonstrated that 1,2,5,*x*-tetrachloronaphthalene (m.p. 164°) is iden-

TABLE 6

DETAILS OF THE SYNTHESIS OF PCNs NOT PREPARED ACCORDING TO REACTION SCHEMES 1–3 IN TABLE 5

PCN	*Starting product*	*Method*	*Reference*
	Tetralin		
1,2,3	1,1,2,3,4-Pentachlorotetralin	Boiling with C_2H_5ONa	19
1,2,3,4	1,1,2,3,4,4-Hexachlorotetralin	Boiling with C_2H_5ONa	19
	Nitro derivative		
1,2,6,8	1,2,6,8-Tetranitronaphthalene	PCl_5 and some $POCl_3$ at 180°	34
1,4,5,8	4,8-Dichloro-1,5-dinitronaphthalene	PCl_5	35–37
1,2,3,5,*x*	1,2,3,5-Tetrachloro-*x*-nitro-naphthalene	PCl_5	37, 41
1,3,5,8,*x*	1,3,5,8-Tetranitronaphthalene	Conc. HCl at 240°	42
1,2,3,4,5,6	1,2,3,4,5,6-Hexachloro-7-nitro-naphthalene	(1) Zn–acetic acid; (2) $NaNO_2$; (3) H_3PO_2	43
	Quinone		
1,2,3,4,5	2,3-Dichloro-1,4-naphthoquinone	PCl_5 and some $POCl_3$ at 180–200° or PCl_5 only at 200–250°	39, 40
	Miscellaneous		
x,*x*,*x*,*x*	Dichloronaphthalene	(1) Chlorination; (2) KOH	38
2,3,6,7	2,3,6,7-Tetrachloronaphthalene-tetracarboxylic acid	Basic copper carbonate in quinoline at 240°	38
1,2,4,5,6,8	1,3,5,7-Tetrachloro-4,8-bistosyl-aminonaphthalene	(1) H_2SO_4; (2) $NaNO_2$; (3) HCl + $CuCl_2$	38
1H-hepta	Octachloronaphthalene	$LiAlH_4$	44, 45
2H-hepta	Halowax 1051	Fractional crystallization	44, 45
Octa	See text and ref. 46 for details		

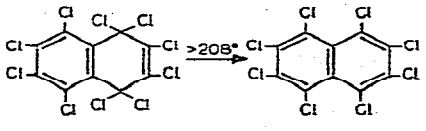
tical with 1,2,5,6-tetrachloronaphthalene. Hardy *et al.*[32] have confirmed that the 1,2,7,*x*-tetrachloronaphthalene synthesized by Turner and Wynne indeed has $x = 4$, as already suggested by Wynne[52]. Lastly, the *x*,*x*,*x*,*x*-tetrasubstituted PCN mentioned in Table 6 has been isolated[38] from the oily by-product obtained in the synthesis of 1,2,3,4,5,8-hexachlorotetralin by chlorination of crude dichloronaphthalene, followed by treatment with alcoholic potassium hydroxide. The unknown structures of the various pentachloronaphthalenes recorded in Tables 5 and 6 have not yet been elucidated.

(d) Hepta- and octa-PCNs

Recently, Clark and co-workers[44,45] described the preparation of a pure heptachloronaphthalene (probably 1H-heptachloronaphthalene) by reduction of octachloronaphthalene with aluminium lithium hydride. The other, still impure, heptachloro isomer has been obtained by fractional crystallization of Halowax 1051 from toluene and carbon tetrachloride. The assignment of structures to the heptachloronaphthalenes is discussed in Section III.

Octachloronaphthalene is prepared by exhaustive chlorination of naphthalene with, for example, chlorine and phosphorus(V) chloride[53], or chlorine, iron and iodine at 100–150°[16,54]. Nearly quantitative yields are realized[55] in vapour-phase chlorination using *e.g.* charcoal or rhodium(III) chloride–alumina at 300°. A short survey of the literature on perchlorination was given by Suschitzky[56], while a discussion on the use of perchlorination for PCN analysis is presented in Section III.2.

Lastly, it should be noted that decachloro-1,4-dihydronaphthalene is obtained in good yield from Halowax 1014[46] or a 1-phenylmethylnaphthalene derivative[57] and a mixture of disulphur dichloride, sulphuryl chloride and aluminium trichloride. When decachloro-1,4-dihydronaphthalene is heated above its melting point (208°), octachloronaphthalene is formed:



(2)

It has been suggested[46] that such a thermal reaction may account for the fact that both compounds give an identical mass spectrum (corresponding to that of octachloronaphthalene) and display identical retention times in gas–liquid chromatography (GLC).

(e) Deuterated compounds

The synthesis of partly deuterated naphthalenes and octadeuteronaphthalene[58], their main physical properties[58] and IR[59] and Raman[58] spectra have been reported.

(f) Melting points

The melting point data of the disubstituted PCNs have been analyzed by De Laszlo[60]. The α,β-dichloronaphthalenes, which exhibit no degree of symmetry, have lower melting points than have the β,β- and α,α-dichloronaphthalenes, all of which possess a plane of symmetry. The di-β-substituted isomers melt at higher temperatures than do the di-α-substituted isomers, and 2,6-dichloronaphthalene, which has its substituents in positions analogous to those in *para*-substituted benzenes, has the highest melting point. The same sequence is observed for the corresponding dibromonaphthalenes.

3. General properties and uses

Most information is available on the Halowaxes and Nibren waxes and these particular types will therefore serve for further discussion[6,13,14,17] of PCNs in general.

(a) Properties

As is evident from the data in Section II.1, except for Halowaxes 1031 and 1000, the commercially available PCN mixtures can be described as having chlorine contents from 40 to 70 wt.-%, melting points in the range 80–185°, specific gravities (at ambient temperature) from 1.5 to 2.0, dielectric constants of 4.5 ± 1, and direct-current resistivities of about $10^{14}\ \Omega\cdot$cm at room temperature and $10^{11}\ \Omega\cdot$cm at their melting points.

The chlorinated naphthalenes are excellent dielectrics and possess a high degree of chemical stability, indicated by their resistance to concentrated bases and acids, except concentrated nitric acid. PCN mixtures remain stable even at temperatures up to their boiling range, and are stable to oxidising agents. At 120–125°, they are unaffected by copper and mild steel in a dry atmosphere, and at 40–50° in the presence of moisture. In the presence of moisture at 120–125°, they tarnish copper, owing to the liberation of small amounts of hydrogen chloride. Other desirable characteristics include inherent flame resistance and resistance to fungus growth. The solid products melt to liquids of extremely low viscosity.

Chlorinated naphthalenes are generally compatible with petroleum waxes, chlorinated paraffins, polyisobutylenes, low-molecular-weight styrene, phenolic resin solutions and several plasticizers. They have limited compatibility with ethylcellulose, polyethylene and vinyl resins, and are not compatible with nitrocellulose or cellulose acetate.

PCNs have good solubility in chlorinated and aromatic solvents and in petroleum naphthas. They have limited solubility in ketones, ethers, acetates and mineral oils, and are insoluble in alcohols and water.

The toxicity of the PCNs, which is discussed in Section IV.1, calls for special precautions in their use. Poisoning by PCNs may take the form of acne or of toxic jaundice. Systematic poisoning is a consequence of inhalation of the fumes from the molten substances, rather than from handling the cold solids. Damage from inhaling the fumes can be severe and occasionally fatal. Before being employed on work with PCNs, one should undergo a medical examination in order to ascertain whether one has suffered or is suffering from any disease that affects the liver, as it is known that such persons are predisposed to further liver damage by PCN poisoning.

The principal precautionary measures to be taken against PCN poisoning are the provision of forced ventilation, washing facilities and protective clothing, which should be dry-cleaned frequently. The use of barrier creams, to be applied to the hands before working with chlorinated naphthalenes, has also been recommended. After handling PCNs, one should wash with soap and apply lanolin to the skin. For general precautions to be taken when using PCNs industrially, the reader is referred to a paper by Greenburg[61].

1-Monochloronaphthalene is the only pure PCN that is liquid at ordinary temperatures. It is miscible with most of the common organic solvents and, at moderate temperatures, is unaffected by water and alkali and has no corrosive action on the common materials of construction. So far, 1-monochloronaphthalene has not been reported to have the harmful effects associated with the higher chlorinated naphthalenes. However, it is recommended that contact with the skin should be avoided and adequate ventilation should be provided.

(b) Uses

PCN mixtures are used chiefly in the electrical industry, *e.g.*, as separators in storage batteries, as capacitor impregnants and as high-temperature and flame-resistant seals for condensers and coils. They are also employed as binders for electrical-grade ceramics and sintered metals. PCNs, as the molten wax or in the form of emulsions, are used in cable-covering compositions, and to impregnate wood, paper and textiles, to which they impart water-proofness, flame resistance and

fungicidal and insecticidal properties. Some grades of PCN mixtures, and 1-monochloronaphthalene, have been applied as insecticides.

When compounded with materials such as resins, rubber, plastics, talc, kaolin and PCBs, the PCNs form a wide range of mouldable masses of appropriate hardness, plasticity, etc. Further, PCNs are used to dissolve sludge and varnish formed by petroleum oils and as ingredients in motor tune-up compounds and photoelastic immersion fluids. They are employed as plasticizers, as additives in automobile and industrial gear oils and cutting oils, and in protective coatings, lacquers and underwater paints. Halowax 1051 is used in organic fillers when flame retardancy is required, and Halowax 1031 has been suggested as a raw material for dyes. The PCN waxes are easily coloured, *e.g.*, with Ceres dyes.

III. ANALYSIS

1. Chromatography

Armour and Burke[62] were among the first workers to study the behaviour of PCNs in view of their possible interference in the analysis of organochlorine pesticides and/or PCBs. They demonstrated that under the GLC conditions used for the analysis of organochlorine pesticide residues[63], Halowax 1099 and 1014 exhibit peaks throughout the retention-time region of the pesticides (retention time relative to aldrin, 0.5–6); the highly chlorinated Halowax 1051 is eluted beyond the retention times of the common pesticides (retention time relative to aldrin, 11). A study of Florisil column-chromatographic clean-up[63] showed that Halowax 1014, 1099 and part of Halowax 1051 are eluted by 200 ml of 6% diethyl ether in light petroleum, which also elutes pesticides such as DDT and its analogues. Recovery studies with Halowax 1014 (50 μg added to 100-g samples of fish, milk and spinach) using the FDA method[63] revealed recoveries of 67, 68 and 90%, respectively. According to the authors, the low recoveries from fish and milk resulted from unfavourable partitioning between light petroleum and acetonitrile.

As an alternative, Armour and Burke carried out chromatography on a silica gel (+3% added water)–Celite (4:1, w/w) column, using the procedure reported in ref. 64. All Halowaxes tested were completely eluted by the 250 ml of light petroleum used as eluent, in which fraction PCBs were also recovered. No Halowax was found in the subsequent 200-ml acetonitrile–*n*-hexane–dichloromethane (1:19:80, v/v) mixture, which contained most of the common organochlorine pesticides (Fig. 2). The recovery of Halowax 1014 added to a trout sample (50 μg to 10 g of fish) was over 90%. The procedure, which has also been recommended by Goerlitz and Law[65], suffers from the disadvantage that large volumes of solvents (*ca.* 0.5 l per sample) are required.

Separation of PCNs plus PCBs from organochlorine pesticides also occurs in the alumina–silica gel column-chromatographic procedure developed by Holden and Marsden[66] and modified by Zitko[67]. A summary is given in Table 7. Both PCNs and PCBs are eluted in fractions I and II; *p,p'*-DDE is also partly eluted in the *n*-hexane fractions, but separation from most other common pesticides is successful. Zitko emphasized that in order to achieve reproducible chromatographic conditions, the activity of the adsorbents must be carefully controlled, the activation procedures described in detail, and the quality of the solvents used for elution specified.

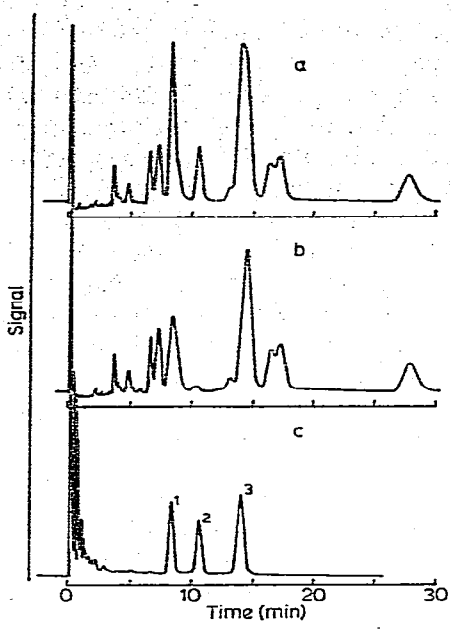


Fig. 2. GLC of brown-trout Florisil column eluate fortified with 2.5 ppm of Halowax 1014, 0.3 ppm of *p,p'*-DDT and 0.2 ppm of *p,p'*-TDE and containing 0.19 ppm of *p,p'*-DDE residue. (a) Before separation. (b) Light petroleum eluate from silica gel column. (c) Polar eluate from silica gel column containing (1) *p,p'*-DDE, (2) *p,p'*-TDE and (3) *p,p'*-DDT. A 10-mg sample was injected for each curve. For GLC conditions, see ref. 62.

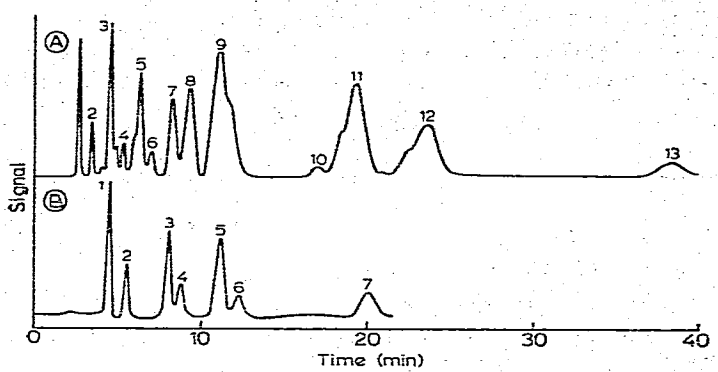
As an alternative method for the discrimination between PCNs and other types of organochlorine compounds, Gulan *et al.*[68] trapped the components of a mixture as they were eluted from the gas chromatograph (2% SE-30–2% QF-1 on 70–80-mesh Anakrom ABS at 180°), added a small amount of *n*-hexane, exposed the solution to the light from a 100-W, medium-pressure UV lamp and re-chromatographed the irradiated products on a 4% SE-30–4% QF-1 on 70–80-mesh Anakrom ABS column, the temperature being programmed from 170° to 190°. As an illustra-

TABLE 7

PROCEDURE FOR SEPARATION OF PCNs AND PCBs FROM ORGANOCHLORINE PESTICIDES[66,67]

Step	*Procedure*
1	Sample (5 g) ground with anhydrous Na_2SO_4
2	Ground sample extracted with pesticide-grade *n*-hexane, Soxhlet, 1 h, final volume of extract 100 ml
3	Chromatography on alumina (Fisher No. A-540), aliquot of extract (1–50 ml) in 1.5 ml of *n*-hexane, alumina activated at 800° (4 h), 5% water added. Column 45 × 0.7 cm, 2 g of alumina, 20 ml of effluent collected
4	Chromatography on Silicar silica gel. Effluent from alumina in 1.5 ml of *n*-hexane, Silicar activated overnight at 130°, 3% water added, column 45 × 0.7 cm, 2 g of Silicar
5	Effluent: *n*-hexane, 10 ml: fraction I; 20 ml: fraction II; 10% diethyl ether in *n*-hexane, 10 ml: fraction III

tion, data on the so-called optimal irradiation time (*i.e.*, the minimal time that yields about equal areas for the main degradation peak and for the parent peak) of the 13 peaks obtained on GLC of Halowax 1014, and the fingerprint degradation patterns observed after re-chromatography, are shown in Fig. 3. The insecticides heptachlor, aldrin, heptachlor epoxide, *o,p'*- and *p,p'*-DDE, dieldrin and *o,p'*- and *p,p'*-DDT, which interfere in GLC, can easily be distinguished from the Halowax peaks 3, 4,



C

Peak no.	Optimum irradiation time (sec)	GLC degradation pattern
1	—	
2	300	
3	145	
4	142	
5	160	
6	60	
7	90	
8	150	
9	210	
10	5	
11	240	
12	35	
13	10	

Fig. 3. GLC (ref. 68) of (A) Halowax 1014 and (B) a mixture of insecticides: (1) heptachlor, (2) aldrin, (3) heptachlor epoxide, (4) *o,p'*-DDE, (5) *p,p'*-DDE, (6) dieldrin and *o,p'*-DDD, (7) *p,p'*-DDT. (C) Irradiation procedure and degradation patterns of peaks 1–13 of Halowax 1014 presented as peak area *versus* $t_{ret.}$. P = parent peak. Trapping GLC on 2% SE-30–2% QF-1 on 70–80-mesh Anakrom ABS. Temperatures: injection and detector (^{3}H), 200°; oven, 180°. Gas flow-rate, Ar–CH_4 (19:1), 60 ml/min. Re-chromatography on 4% SE-30–4% QF-1 on 70–80-mesh Anakrom ABS. Temperatures: injection, 240°; detector, 210°; programmed from 170° to 190° at 2°/min. Gas flow-rate, N_2, 30 ml/min.

7–9 and 11, as their degradation products are largely resolved from those of the PCN degradation products. The authors claim that the same holds true for the PCB mixture Aroclor 1254 for all but one pair of corresponding GLC peaks.

Goerlitz and Law[65], who also studied the extent to which PCNs may interfere in the analysis of pesticides, presented chromatograms of Halowax 1013 and 1014, analyzed by electron-capture GLC on 3% OV-101 (on Gas-Chrom Q) and 3% OV-101–5% OV-210 (on Gas-Chrom Q) columns at 180° and 175°, respectively. Identification of the chlorine content of the peaks was achieved with the aid of a computer-controlled GLC–mass spectrometry (MS) system. Fig. 4 shows representative chromatograms and the chlorine-number assignments of each peak. According to the authors, the pattern of compounds and isomers of a particular PCN preparation, as it appears on the chromatogram, is not as characteristic or distinctive as that of PCB formulations. In other words, one cannot readily assess the occurrence of PCNs in previously analyzed samples simply by reviewing the chromatographic records.

The combined use of thin-layer chromatography (TLC) and GLC for the analysis of PCNs has been proposed by Stalling and Huckins[69]. The components of Halowax 1099, 1013 and 1014 were resolved by reversed-phase TLC on Kieselguhr-coated glass plates impregnated with paraffin oil. Three successive developments were carried out in a saturated atmosphere, using methanol–acetonitrile–acetone–water

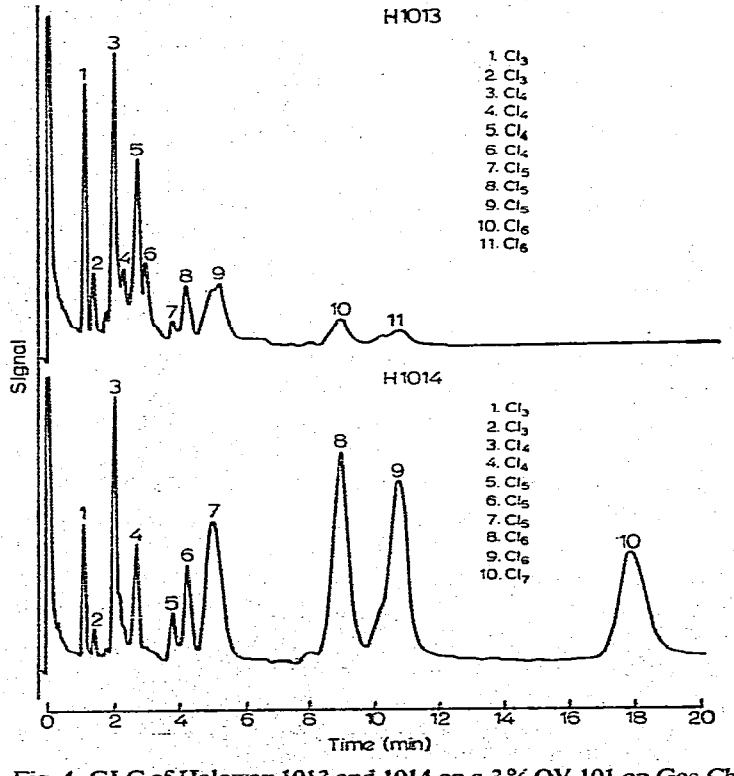


Fig. 4. GLC of Halowax 1013 and 1014 on a 3% OV-101 on Gas-Chrom Q column[65]. Temperatures: injection, 205°; column, 180°; detector (^3H), 200°. Gas flow-rate, N_2, 37 ml/min; He used instead of N_2 in GLC–MS.

(8:8:3:1, v/v) saturated with paraffin oil as the mobile phase. Identification was effected by spraying with a solution of silver nitrate (1.7 g) in ethanol (200 ml) to which ammonia solution (sp.gr. 0.880) (1 ml) is added just before application. The plate was then held over a steam-bath for a few seconds and finally placed under a UV lamp for several minutes. All chlorinated components appeared as dark spots on a light background. Approximately 8–15 μg of the Halowaxes are required in order to detect the major components. In order to relate the TLC data to results obtained by GLC, they eluted the pertinent zones on the chromatogram with light petroleum–diethyl ether (19:1, v/v) and analyzed the resulting solutions on a 0.3% OV-7 on glass beads column at 160 or 190°, using a nickel-63 electron-capture detector. Temperature-programmed GLC–MS was used to characterize Halowax standards in terms of the chlorine contents of the individual peaks. From the results, which are summarized in Table 8, it is apparent that spots with lower R_F values generally correspond to GLC peaks with longer retention times, *i.e.*, to Halowax components with more chlorine atoms. Stalling and Huckins[69] also presented gas chromatograms of Halowax 1031, 1000 and 1051, but did not comment on them.

According to Brinkman *et al.*[70], reversed-phase TLC of PCNs on Kieselguhr

TABLE 8

CORRELATION OF REVERSED-PHASE TLC SPOTS AND GLC PEAKS OF HALOWAX 1099, 1013 AND 1014[69]*

Halowax	R_F *in TLC***	*Retention time relative to aldrin or p,p'-DDE in GLC****	*GLC–MS*	
			No. of Cl atoms	*Mol. wt.*
1099	0.52	1.97	5	298
	0.67	0.83, 1.03	4	264
		2.48, 2.82	5	298
	0.77	1.18	4	264
	0.81	0.44, 1.28	3, 4	230, 264
	0.85	1.53, 0.62	4, 3	264, 230
	0.89	0.23	2	196
1013	0.46	1.67, 4.64	5	298
	0.50	4.98, 5.70	6	332
	0.58	0.70, 1.97	4, 5	264, 298
	0.66	0.82, 1.02	4	264
		2.48, 2.82	5, 6	298, 332
	0.76	1.27	4	264
	0.81	1.52, 0.43	4, 3	264, 230
	0.85	0.60	3	230
1014	0.35	1.60, 1.89, 4.21	6, 7	332, 366
	0.44	0.72, 0.84	5	298
		1.98, 2.28	6	332
	0.56	0.30, 2.53	3, 6	230, 332
	0.61	0.38, 1.05, 1.19	4, 5	264, 293
	0.81	0.23, 0.58	4, 3	264, 230

* For TLC and GLC conditions, see text and subsequent notes.

** R_F for *p,p'*-DDE, 0.92.

*** Column temperature, 160° (Halowax 1099 and 1013) or 190° (Halowax 1014); retention times relative to aldrin (Halowax 1099 and 1013) or *p,p'*-DDE (Halowax 1014).

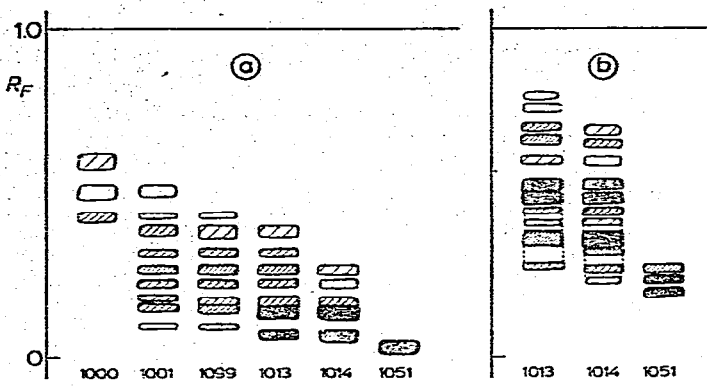


Fig. 5. TLC of Halowax 1000–1051 on (a) Kieselguhr impregnated with paraffin oil/acetonitrile–methanol–water (8:9:3); (b) Kieselguhr impregnated with paraffin oil/acetonitrile–methanol–acetone–water (20:20:9:1)[70]. Detection: spraying with a solution of 0.3% tolidine in 80% ethanol containing 0.3% glacial acetic acid and subsequent UV irradiation.

impregnated with paraffin oil is superior to TLC with the system silica gel–dry *n*-hexane (*cf.* ref. 176). With the former technique (Fig. 5), about twice as many spots are observed. Acetonitrile–methanol–water (8:9:3, v/v) is recommended for the separation of the low-chlorinated Halowaxes; improved resolution of the more highly chlorinated mixtures is obtained with acetonitrile–methanol–acetone–water (20:20:9:1, v/v) as the mobile phase. The data compare favourably with those of Stalling and Huckins[69], who reported the presence of 5–7 spots in the reversed-phase TLC of various Halowaxes (Table 8). The excellent separation obtained with Halowax 1051 is discussed below.

Challen and Kučera[71] studied the detection of PCNs and other commercial wood preservatives using TLC and GLC. With chloroform extracts of wood (46 species), the several preservatives were separated best on silica gel with *n*-hexane–ethyl acetate (17:3, v/v) as the mobile phase. Spraying with a 0.1% solution of diiodofluorescein in alcohol, and subsequent exposure to bromine vapour, allowed the detection of 50–100 μg of PCNs. In GLC, the large number of peaks observed with samples containing PCNs allows their detection; however, it renders impossible their identification in mixtures with other preservatives.

An extensive study on the identity of the PCNs present in Halowax 1031, 1000, 1001 and 1099 was reported by Beland and Geer[8]. Chromatograms were run on two different columns, *viz.*, a 10% Carbowax 20M on 60–80-mesh Chromosorb W and a mixed 5% Bentone 34–10% OV-101 on 100–120-mesh Supelcoport column, using an oven temperature of 180° (Fig. 6). From the data collected in Table 9, it can be seen that both monochloronaphthalenes were found to be present, together with all of the disubstituted isomers (except 2,6-dichloronaphthalene) and several of the possible tri- and tetrasubstituted naphthalenes. In addition, at least three components appear to be present that do not seem to be PCNs. Four PCNs identified in Halowax 1001 have also been shown[72] to be present in Nibren D88, which has a comparable chlorine content. A sample of Nibren D88 was separated into 22 fractions on a column of activated alumina, using light petroleum as solvent and light petroleum–benzene (99:1, v/v) as the mobile phase. Detection by means of IR absorption measurement indicated

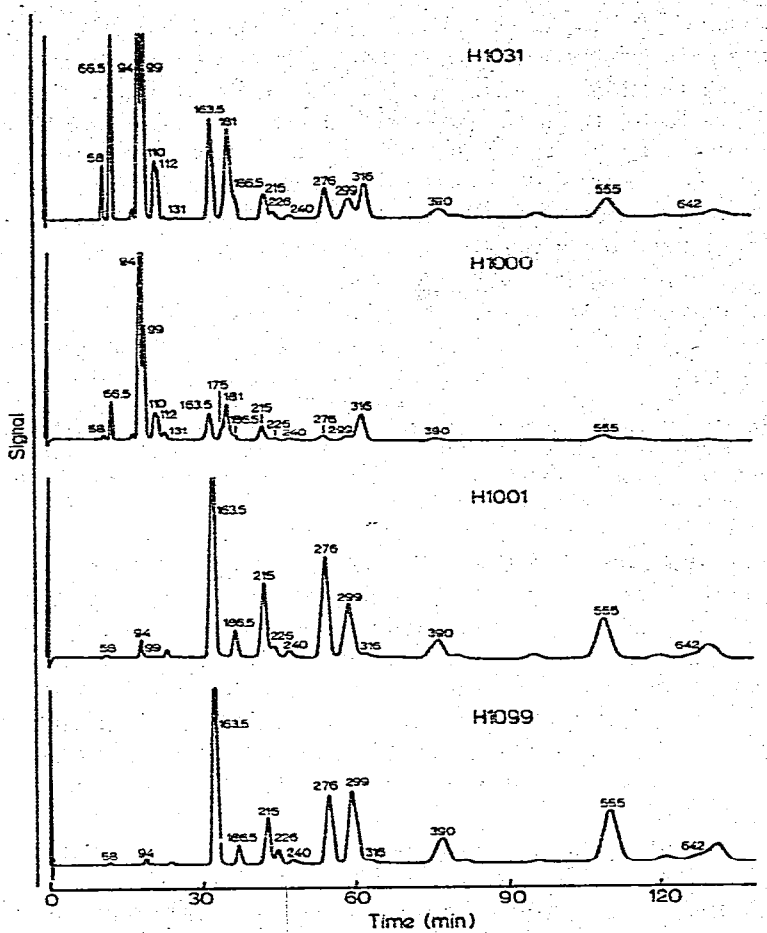


Fig. 6. GLC (ref. 8) of Halowax 1031 (3 μg), 1000 (0.3 μg), 1001 (30 ng) and 1099 (30 ng) on a Bentone 34–OV-101 packed column. Temperatures: injection, 190°; oven, 180°; detector (^{3}H), 190°. Gas flow-rate, N_2, 30 ml/min.

that the first three fractions contained 1,3,5,7-tetrachloronaphthalene, and that 1,4,6-trichloro-, 1,4,5-trichloro- and 1,4,5,8-tetrachloronaphthalene were the main components of fractions 4–9, 10–15 and 16–22, respectively.

Beland and Geer[8] pointed out that electron-capture gas chromatograms give misleading values of the amounts of each individual PCN present. They observed that an increase in the detector response occurs largely in the mono- to trichloro range, although the magnitude of the effect is not yet known. For instance, Halowax 1031 contains a minimum of 96% of monochloronaphthalenes, yet the chromatogram in Fig. 6 shows a clear indication of tetrasubstituted isomers being present, although at very low concentrations.

High-performance liquid chromatography (HPLC) in the system silica gel–dry *n*-hexane has been used[70] to characterize the behaviour of three series of commercially available PCN mixtures, *viz.*, Halowax 1031–1051, Nibren D88–D130 and Clonacire 90–130. Chromatograms of the Halowax series are presented in Fig. 7; they were re-

TABLE 9

RETENTION TIMES AND IDENTIFICATION OF COMPONENTS OF HALOWAX 1031, 1000, 1001 AND 1099

For GLC details, see text and Fig. 6.

Retention time (min) on		*PCN*	*Halowax*			
Bentone	*Carbowax*		*1031*	*1000*	*1001*	*1099*
58.0	32.0	2	+	+	+	+
66.5	32.0	1	+	+		
94.0	62.0	1,4	+	+	+	+
99.0	62.0	1,5	+	+	+	
110.0	57.0	1,3	+	+		
112.0	69.0	1,6	+	+		
131.0	77.0	2,7	+	+		
163.5	84.0	2,3	+	+	+	+
163.5	108.5	1,4,6	+	+	+	+
175.0	77.0	1,2		+		
181.0	69.0	1,7	+	+		
186.5	94.5	1,3,5	+	+	+	+
215.0	108.5	1,2,4	+	+	+	+
226.0	127.0	1,3,5,7	+	+	+	+
240.0	154.5	1,2,6	+	+	+	+
276.0	199.0	1,4,5	+	+	+	+
299.0	177.0	1,2,4,6	+	+	+	+
316.0	127.0	1,8	+	+	+	+
390.0	254.0	1,3,5,8	+	+	+	+
555.0	526.0	1,4,5,8	+	+	+	+
642.0	272.0	1,2,3,4	+	+	+	+

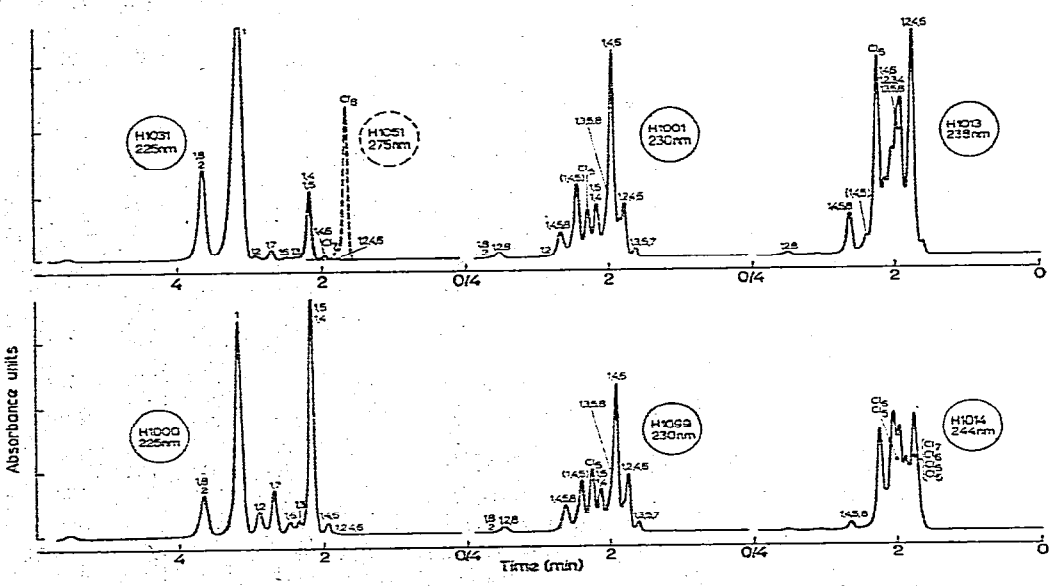


Fig. 7. HPLC (ref. 70) of Halowax 1031–1051 (*ca.* 300 ppm in *n*-hexane). Column, 25 cm × 3 mm I.D. filled with 5-μm LiChrosorb SI 60; mobile phase, dry *n*-hexane; flow-rate, 1.4 ml/min; UV detection at the wavelengths indicated in the figures; full scale, 1.28 (Halowax 1031, 1000, 1001 and 1099), 0.64 (Halowax 1013 and 1014), 2.56 (Halowax 1051) absorbance units; temperature, 27 ± 1°. Tentative assignments are indicated by parentheses.

TABLE 10

HPLC RETENTION TIMES, UV AND IR SPECTRAL DATA AND REDUCTION POTENTIALS OF INDIVIDUAL PCNs AND NAPHTHALENE

Data on HPLC ($t_{ret.}$) and UV spectra taken from ref. 70; for UV spectra of 1,4-di-, 1,5-di- and 1,4,5,8-tetrachloronaphthalene, also see ref. 35, and for those of all mono- and disubstituted PCNs, ref. 60; data on reduction potentials taken from ref. 75; for IR spectra, references have been quoted only.

Substituted PCN	$t_{ret.}$ *(min)*	$\lambda_{max.}$ *(nm)* *	
		B_b band	*L_a band*
Naphthalene	5.40	218s, 221	257, 265, 274, 285
1	3.15	219s, 223	264, 273, 284, 295
2	3.60	221s, 225	257, 267, 277, 288
1,2	2.90	215s, 218s, 224s, 230	267, 275, 285, 297
1,3	2.30	214s, 225s, 229	267, 276, 286, 297
1,4	2.15	213s, 224	272, 281, 292, 309
1,5	2.15	217s, 223s, 227	272, 281, 292, 309
1,6	2.45		
1,7	2.65		
1,8	3.65	217s, 220s, 226s, 230	274, 285, 295, 307
2,3	3.30	216s, 220s, 225s, 230	263, 272, 283, 294
2,6	2.80	215s, 219s, 226s, 230	259, 268, 277, 288
2,7	2.80	216s, 221s, 228s, 231	262, 270, 280, 290
1,2,3	2.55	217s, 230s, 234	268, 278, 289, 300
1,2,4			
1,2,5	2.00	216s, 221s, 228s, 233	272, 282, 293, 304
1,2,6	2.35	217s, 230s, 234	264, 274, 284, 296
1,2,7	2.60	220s, 223s, 229s, 234	268, 278, 289, 302
1,2,8	3.50	218s, 231s, 235	275, 287, 298, 310
1,3,5			
1,3,6	2.00	219s, 230s, 234	268, 279, 290, 302
1,3,7	2.15	217s, 222s, 229s, 234	260, 274, 284, 296
1,3,8	2.70	217s, 222s, 230s, 235	275, 287, 298, 311
1,4,5			
1,4,6	1.95	217s, 222s, 227s, 233	275, 285, 296, 309
1,6,7			
2,3,6	2.75	220s, 230s, 235	263, 273*, 284, 295
1,2,3,4	1.95	227s, 232, 238	274, 285, 296, 309
1,2,3,5	1.90	240	276, 287, 298, 311
1,2,3,7	2.35	227s, 237, 240	270, 280, 290, 303
1,2,4,6	1.75	221s, 235s, 237	275, {286 / 291**}, {298 / 303'}, 310
1,3,5,7	1.60	220s, 227s, 233, 239	279, {287 / 291**}, {300 / 303'}, 311
1,3,5,8	2.00	221s, 238	285, 297, 308, 321
1,3,6,7	2.05	223s, 233s, 239	{268 / 273'}, {280 / 284'}, {291 / 296'}, 303
1,4,5,8	2.60	223s, 234s, 238	294, 307, 321, 336
1,4,6,7	1.90	223s, 228s, 241s, 245	280, 290, 302, 314
1,2,3,5,7	1.65	220s, 226s, 238s, 244	{272 / 279'}, {284 / 290'}, {296 / 301'}, {309 / 314'}
1,2,3,6,7,8			
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.

Reduction potentials, E_{2a} vs. S.C.E. (V)									*Ref. on IR*
−2.326	−2.197								
−2.326	−1.940								76
−2.326	−1.975								76
−2.326	−1.957	−1.726							72
−2.326	−1.965	−1.752							72
−2.326	−1.944	−1.751							72, 77
−2.326	−1.933	−1.765							72, 77
−2.326	−1.948	−1.802							72
−2.326	−1.944	−1.793							72
−2.326	−1.938	−1.704							72
−2.326	−1.960	−1.769							72
−2.326	−1.957	−1.844							72, 77
−2.326	−1.959	−1.838							72
−2.326	−1.975	−1.761	−1.554						72
−2.326	−1.939	−1.752	−1.565						72
−2.326	−1.942	−1.783	−1.581						72
−2.326	−1.955	−1.827	−1.620						72
−2.326	−1.955	−1.898	−1.613						72
−2.326	−1.941	−1.785	−1.512						72
−2.326	−1.938	−1.781	−1.578						72
−2.326	−1.958	−1.824	−1.634						72
−2.326	−1.974	−1.853	−1.635						72
−2.326	−1.960	−1.806	−1.541						72
−2.326	−1.932	−1.758	−1.540						72
−2.326	−1.941	−1.776	−1.618						72
−2.326	−1.938	−1.778	−1.599						72
−2.326	−1.956	−1.820	−1.657						72
−2.326	−1.946	−1.751	−1.563	−1.393					72
−2.326	−1.948	−1.784	−1.591	−1.411					72
−2.326	−1.959	−1.832	−1.627	−1.445					72
−2.326	−1.954	−1.783	−1.609	−1.445					72
−2.326	−1.960	−1.836	−1.615	−1.444					72
−2.326	−1.946	−1.783	−1.616	−1.373					72
−2.326	−1.955	−1.782	−1.607	−1.490					72
−2.326	−1.929	−1.755	−1.535	−1.345					72, 77
−2.326	−1.957	−1.729	−1.576	−1.431					72
−2.326	−1.985	−1.833	−1.639	−1.506	−1.340				—
									77
−2.326	−2.028	−1.840	−1.706	−1.600	−1.411	−1.298	−1.081	−0.940	59, 72, 77

corded at or near the wavelength of maximum absorption. Nibren D88 and Clonacire 90 display chromatograms, as well as melting points and UV spectra (*cf.*, Sections II.1 and III.3), that are virtually identical with those of Halowax 1001. The more highly chlorinated Nibren D116N and Clonacire 115 strongly resemble Halowax 1013; Nibren D130 displays the same behaviour as Halowax 1014. For Clonacire 130, a composition intermediate between those of Halowax 1013 and 1014 was suggested.

Comparison of the chromatograms in Fig. 7 with data on PCBs in ref. 73 reveals that the major peaks of low-chlorinated PCB mixtures are eluted separately from those of all Halowaxes. However, more highly chlorinated PCB mixtures, as well as polychlorinated terphenyls[74] and various common chlorinated pesticides, are eluted in the retention-time region characteristic for PCNs. However, it was demonstrated that detection at two different wavelengths, lying in the 195–215 and 275–320 nm regions, will help to discriminate between, and even determine quantitatively, PCNs and PCBs. The results will be best for PCNs, because PCBs and polychlorinated terphenyls show negligible absorption above 275 nm. 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. In practice, another limitation to the UV approach is the background generated by UV-absorbing compounds eluted from the column material and/or extracted from the sample to be analyzed[67].

Data[70] on the retention times of 33 individual PCNs in the HPLC system silica gel–dry *n*-hexane are presented in Table 10. The retention behaviour appears to be determined by two main effects: (1) increasing introduction of chlorine atoms into the naphthalene nucleus decreases the retention, non-adjacent α-substitution having a greater effect than non-adjacent β-substitution in this respect; (2) substitution in the adjacent 1,8- and, although less so, in the 2,3-positions promotes retention. Illustrative examples are the relatively high retention time of 1,4,5,8-tetrachloronaphthalene compared with those of the 1,4- and 1,5-dichloronaphthalenes, and the very short retention time of 1,3,5,7-tetrachloronaphthalene. With the last PCN, the complete absence of substitution in adjacent positions causes it to move ahead of all PCNs studied, including octachloronaphthalene.

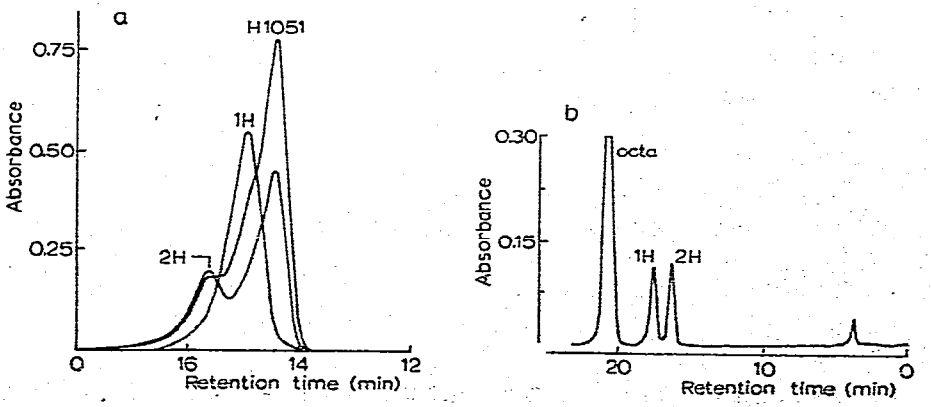


Fig. 8. HPLC (ref. 78) of Halowax 1051 in the systems (a) silica gel–dry *n*-hexane at a flow-rate of 0.2 ml/min (temperature, 27 ± 1°); (b) LiChrosorb RP-8/methanol–water (8.5:1.5) at a flow-rate of 0.9 ml/min (temperature, 20 ± 1°). UV detection at (a) 256 and (b) 230 nm.

TABLE 11

CHROMATOGRAPHIC AND SPECTRAL DATA FOR HEPTA- AND OCTACHLORONAPHTHALENES

Substituted PCN	*R_F in reversed-phase TLC**	*$t_{ret.rel.}$ in GLC**	*$t_{ret.}$ in HPLC (min)**	*$t_{ret.}$ in reversed-phase HPLC (min)**	*$\lambda_{max.}$ (nm)**	*^{1}H-NMR signal (τ)***
1H-Hepta	0.23	0.63	1.70	18.5	256	1.53
2H-Hepta	0.27	0.63	1.80	16	—	2.15
Octa	0.19	1.00	1.65	21	275	—

* Data from ref. 78.
** Data from ref. 72.

In several recent papers[44,70,78], special attention has been devoted to the analysis of Halowax 1051, which is a mixture of octachloronaphthalene (90%) and heptachloronaphthalenes (10%). GLC provides[44,69] a sharp separation of the octa- from the hepta-substituted naphthalene(s), but as yet does not allow the separation of the 1H- from the 2H-isomer. Surprisingly, three separate zones show up in reversed-phase TLC (Fig. 5). HPLC in the system silica gel–dry *n*-hexane also reveals the presence of at least three constituents (Fig. 8a), while an excellent separation occurs in reversed-phase HPLC on a LiChrosorb RP-8 column, using methanol–water (9–8:1–2, v/v) mixtures as the mobile phase (Fig. 8b). Comparison of the NMR and UV spectra and the HPLC retention times of the hepta-substituted isomers with those of related PCNs strongly suggests that the assignments made in Fig. 8 and Table 11 are correct. As a consequence, the isomer produced by reduction of octachloronaphthalene with aluminium lithium hydride (*cf.*, Section II.2) is believed to be the 1H-heptachloronaphthalene.

2. Differentiation of PCNs from PCBs

In the previous section, it has been shown that an efficient separation of PCNs and/or PCBs from a large number of organochlorine pesticides can be achieved if the chromatographic conditions are closely controlled. However, no method has yet been devised for the differential elution of PCNs and PCBs, although HPLC[70], multi-wavelength detection[67,70], UV irradiation[68] and GLC–MS[65] may help to discriminate between these two closely related types of compounds. Several further attempts to differentiate between PCNs and PCBs are discussed below.

Holmes and Wallen[79] treated a mixture of PCNs and PCBs with an excess of chromium trioxide. After reaction for 20 min at *ca.* 100°, examination of an *n*-hexane extract by electron-capture GLC revealed the presence of peaks due to PCB isomers only; the PCNs were apparently oxidized completely. However, one should bear in mind that, according to another study[80], treatment of PCBs with chromium trioxide–sulphuric acid also leads to considerable decomposition of several low-chlorinated PCB isomers.

In order to simplify the analysis of a heterogeneous mixture of PCNs, PCBs and other similar compounds, conversion into a single derivative has often been suggested, *e.g.*, by exhaustive chlorination to give the fully chlorinated product (per-

chlorination), or by removal of all chlorine atoms to obtain the parent hydrocarbon (dechlorination). The former technique is usually preferred, both on account of the high sensitivity of the electron-capture detector (ECD) towards octachloronaphthalene and decachlorobiphenyl, and of the relatively high volatility of naphthalene and biphenyl, which may incur significant losses during treatment and further handling of the samples.

Hutzinger *et al.*[46] carried out perchlorination by heating the PCN mixture, under reflux, with sulphuryl chloride–antimony(V) chloride (9:1, v/v) for 1 h. Octachloronaphthalene was obtained in good yield; however, no accurate data on the percentage conversion have been published. Treatment with a mixture of disulphur dichloride, sulphuryl chloride and aluminium chloride, and subsequent heating at a temperature exceeding 208° in order to convert the initially formed decachloro-1,4-dihydronaphthalene into octachloronaphthalene, may also be recommended. For obvious reasons, perchlorination is usually combined with electron-capture GLC as a method of analysis. Unfortunately, under the conditions normally employed[46,81], octachloronaphthalene and decachlorobiphenyl (resulting from perchlorination of PCBs) have approximately the same retention times. This effect causes serious interference in the simultaneous determination of PCNs and PCBs in their mixtures. However, according to our experience[82], if GLC is carried out on a 4% OV-101 on 80–100-mesh Chromosorb W (HP) column at 260°, decachlorobiphenyl shows a stronger retention than octachloronaphthalene. The relative retention is *ca.* 1.15 and well resolved peaks are obtained for mixtures of octachloronaphthalene and decachlorobiphenyl containing 10–90% (w/w) of either compound. An excellent separation of both fully chlorinated products has also been obtained by HPLC, using the reversed-phase system previously used for the separation of 1H- and 2H-heptachloronaphthalene (*cf.*, Fig. 8); octachloronaphthalene precedes decachlorobiphenyl, and the relative retention and resolution are *ca.* 1.1 and 2.0, respectively.

Perchlorination with chlorine gas in the presence of iodine as a catalyst has been recommended[81] for discriminating chlorodibenzo-*p*-dioxins from PCNs, PCBs and chlorodibenzofurans. In GLC on a 3% XE-60 on 100–120-mesh Chromosorb W (HP) column at 210°, octachlorodibenzo-*p*-dioxin has a longer retention time than have the fully chlorinated naphthalene, biphenyl and dibenzofuran. Perchlorination with disulphur dichloride, sulphuryl chloride and aluminium chloride, followed by chromatography on an alumina column and final analysis by GLC, has been used[83] to verify the absence of chlorodibenzofurans from samples of Halowax 1014 and technical naphthalene.

With dechlorination, Zimmerli[84] has shown that PCB mixtures are quantitatively converted into biphenyl on a partly deactivated palladium catalyst. Under the same conditions, PCNs are converted into naphthalene plus some tetralin. As Zimmerli did not quote quantitative data on the behaviour of PCNs, no meaningful conclusions can be drawn concerning the merit of so-called carbon-skeleton chromatography.

Hutzinger *et al.*[46] stressed that treatment of PCNs with the very powerful perchlorination reagents antimony(V) chloride–iodine and pure antimony(V) chloride leads to extensive degradation of chlorinated naphthalenes, whereas they are the preferred reagents for the perchlorination of PCBs. In our laboratory, this conclusion has been confirmed for Halowax 1000, 1099, 1014 and 1051. Therefore, the powerful

TABLE 12

UV ABSORPTION DATA FOR PCN MIXTURES[70]

Type	$\lambda_{max.}$		Type	$\lambda_{max.}$	
	B_b band*	L_a band		B_b band	L_a band
Halowax			*Clonacire*		
1031	224	274, 284	90	233	295, 304
1000	224	284, 292	115	238	297, 305
1001	233	297, 304	130	238	306
1099	233	298, 305	*Nibren*		
1013	238	306	D88	233	296, 304
1014	244	310	D116N	238	306
1051	275	332	D130	244	313

* log $\varepsilon_{max.}$ = 4.7–4.8 except for Halowax 1031, which has log ε = 5.0.

perchlorination of PCN–PCB mixtures appears to be a promising alternative to the chromium trioxide oxidation technique discussed above.

3. *UV and IR spectrometry*

Apart from an early paper on the UV absorption of dichloronaphthalenes[60], only one systematic study on the UV spectra of PCNs has been published[70]. Data for commercially available mixtures are recorded in Table 12, while results for individual PCNs are included in Table 10. Several spectra are shown in Fig. 9.

In the UV spectra of aromatic hydrocarbons, the B_b band is the most intense

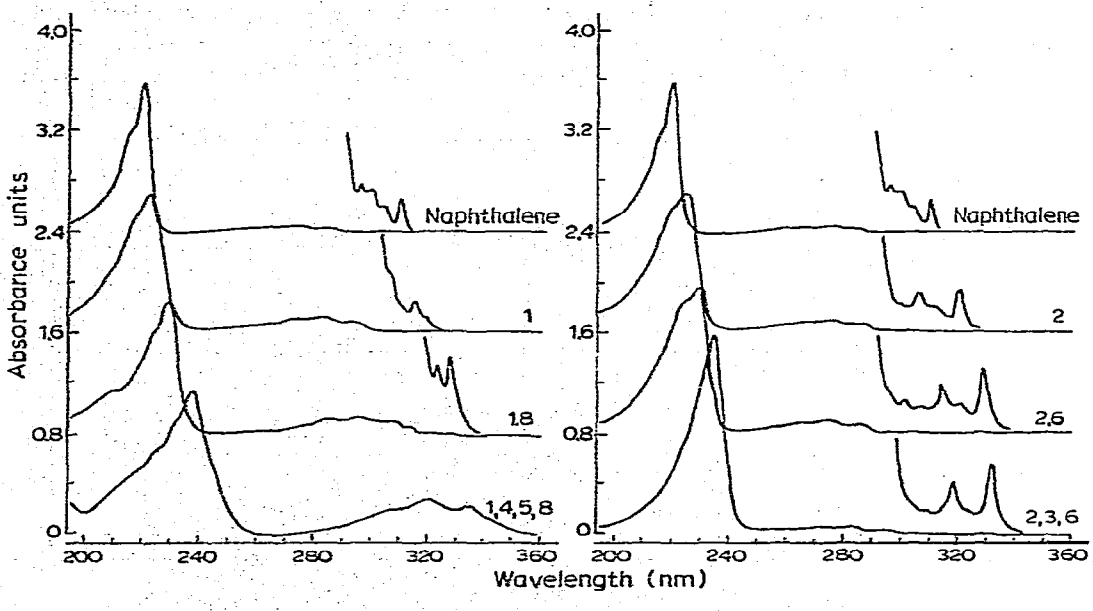


Fig. 9. UV absorption spectra[70] of naphthalene (10 ppm) and 1-mono-, 1,8-di-, 1,4,5,8-tetra-, 2-mono-, 2,6-di- and 2,3,6-trichloronaphthalene (*ca.* 25 ppm in *n*-hexane). Cell pathlength, 2 mm. L_b band, ×60.

(log ε = 4–6). With the PCNs, introduction of chlorine atoms into the naphthalene nucleus induces a bathochromic shift of this band; the magnitude of this shift is chiefly determined by the number, not the positions of the substituents[70]: mono-, 223–225 nm; di-, 224–231 nm; tri-, 233–235 nm; tetra-, 238–245 nm. α-Substitution causes batho- and hyperchromic shifts predominantly in the transverse-polarised L_a band. This effect is clearly demonstrated by comparing the spectra of 1,4-, 1,5- and 1,8-dichloronaphthalene with those of 2,3-, 2,6- and 2,7-dichloronaphthalene. The effect of α-substitution is even more pronounced with the fully α-substituted 1,4,5,8-tetrachloronaphthalene. With β-substituted PCNs, the position of the L_a band hardly changes and, instead, an intensification of the relatively weak L_b band (high-wavelength maxima, 320–330 nm) occurs. These conclusions are in good agreement with the data on disubstituted PCNs published by De Laszlo[60] nearly 50 years ago. Mosby[85] commented briefly on the considerable broadening of the B_b band and the strong bathochromic shift observed in the spectrum of octachloronaphthalene compared with those of less highly substituted PCNs. These features are probably derived to a large extent from the non-planar nature of the fully chlorinated naphthalene.

The IR spectra of PCNs have been studied by Cencelj and Hadži[72], who reported spectra between 1650 and 660 cm^{-1} of the complete range of dichloro- and trichloronaphthalenes and of nine tetrachloronaphthalenes; a selection of these spectra is presented in Fig. 10. Parallel runs with each substance were made in the solid state (Nujol mull) and in solution (carbon tetrachloride and cyclohexane). In most instances there was little difference between the positions of the bands in the solid and the solution state. However, notable exceptions occurred, *e.g.*, with 1,5-, 1,7- and 2,3-dichloronaphthalene, and occasionally there were even differences as regards the number of bands observed. The authors limited the discussion to the 690–900-cm^{-1} region, where a number of strong bands appeared in the spectra of substituted naphthalenes that are known to arise from the out-of-plane deformation vibrations of the hydrogen atoms attached to the rings. Following the method of Thompson[86], Cencelj

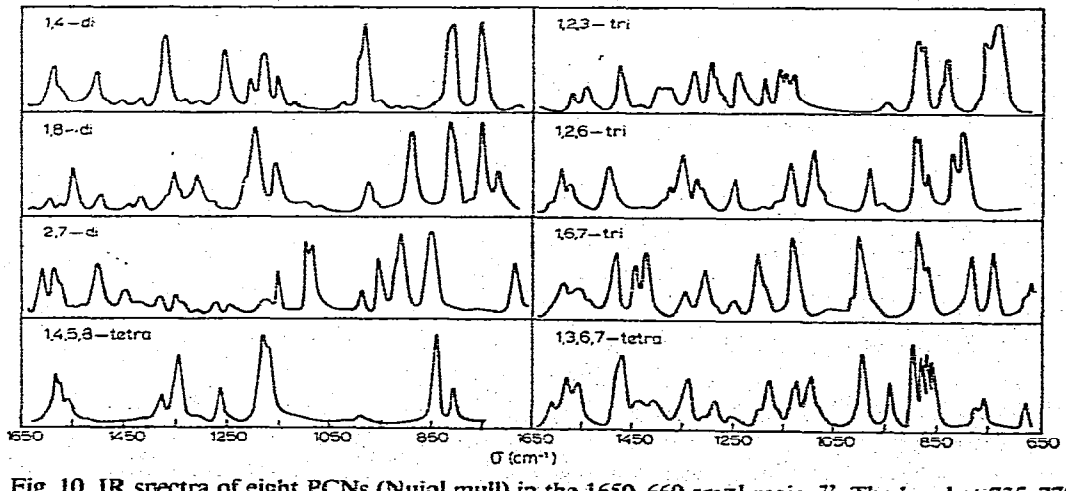


Fig. 10. IR spectra of eight PCNs (Nujol mull) in the 1650–660 cm^{-1} region[72]. The band at 735–770 cm^{-1} is characteristic of four adjacent hydrogen atoms, and a band at 860–900 cm^{-1} is expected to appear for one isolated hydrogen atom (also see ref. 59).

and Hadži[72] quoted several examples that indicate that the pattern of the absorption bands in the above region seems to be characteristic of the types of substitution, and independent of the nature of the substituents. However, there is a serious limitation to the applicability of the correlation rules for the determination of the type of substitution: the presence of a band is not sufficient proof of the presence of the corresponding group of hydrogen atoms. However, the absence of a band required by a particular type of substitution seems to exclude it (*cf.*, Fig. 10 and ref. 87).

Kalmykova *et al.*[77] also noted that changes in the shape of the IR spectra are due to changes in the shape of the molecule and the nature of the spin–orbit interactions. To quote an example, from analysis of IR spectra (1650–150 cm^{-1}) recorded at room temperature, and electronic spectra measured at 4 °K, they concluded that the coplanar nature of 1,4,5,8-tetrachloronaphthalene is significantly disrupted. Remarkably, 1,2,3,6,7,8-hexachloronaphthalene turned out to be planar, while the fully substituted octachloronaphthalene was non-coplanar, although its deformation vibrations were not as intense as those of 1,4,5,8-tetrachloronaphthalene.

The IR spectrum of octachloronaphthalene in carbon disulphide and in potassium bromide (3000–650 cm^{-1}) was studied by Luther *et al.*[59]. They reported frequency assignments made on the basis of a comparison with octadeuteronaphthalene and the system benzene–hexachlorobenzene.

A list of IR spectra of PCNs recorded in the literature, and the pertinent references, are included in Table 10.

4. Mass spectrometry

The mass and ion kinetic energy (IKE) spectra of the two isomeric mono- and several dichloronaphthalenes have been recorded by Safe and Hutzinger[88]. Pertinent data are given in Table 13. The primary ion mass spectra of 1- and 2-monochloronaphthalene are similar, and the fragmentation pattern shows loss of both Cl· and C_2H_2 from the molecular ion. The IKE spectra of both compounds are also identical

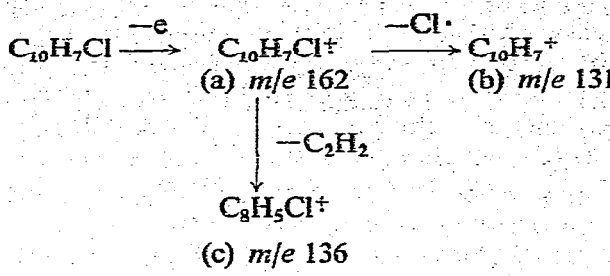
TABLE 13

PRIMARY ION MASS AND IKE SPECTRA INTENSITIES OF MONO- AND DICHLORONAPHTHALENES*

PCN	*Primary ion mass*				*IKE*			
	M	*M − Cl*	*M − C_2H_2*	*M − Cl_2*	*0.867E*	*0.821E*	*0.782E*	*(0.867E)/(0.821E)*
1	100	20	<1					
2	100	18	<1					
1,2	100	11	<1	18	10.5	100	54	0.105
1,3	100	12	<1	20	10.5	100	54	0.105
2,3	100	14	<1	25	11.0	100	55	0.110
1,4	100	11	<1	19	10.5	100	54	0.105
1,5	100	12	<1	21	10.0	100	55	0.100
1,7	100	14	<1	18	10.5	100	56	0.105
1,8	100	14	<1	19	10.0	100	54	0.100

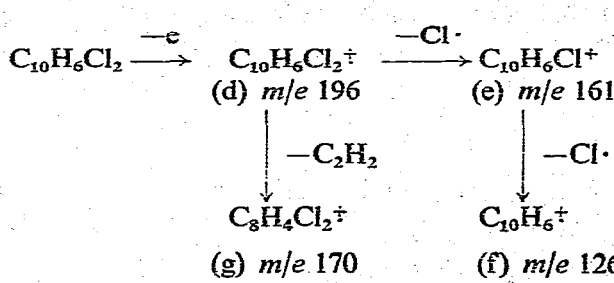
* Recorded[88] at 70 eV, 80 kV with a DuPont CEC-21-110B instrument.

with daughter ion peaks at 0.840 and 0.785 E (ratio, 0.13), corresponding to the reactions a → b and a → c:



These results are evidence of chlorine randomization, at least in the substituted ring of the naphthalene nucleus.

For the disubstituted PCNs, the relative intensities of both the primary ion and IKE spectra are similar for all of the isomers studied. Moreover, the ratios obtained for the two daughter ion peaks resulting from unimolecular decomposition of the molecular ion (0.867 *E*/0.821 *E*) are also virtually indistinguishable; the fragmentation pattern is as follows:



The results suggest that chlorine randomization occurs over all of the carbon atoms in the naphthalene nucleus. This suggestion contrasts with the conclusion of Safe *et al.*[89] concerning IKE spectra of PCB isomers: with substituted biphenyls, the relative peak abundances are different for each isomer and therefore are thought to be of some use in structure analysis.

Mass spectra have been recorded for tri- to heptachloronaphthalenes[65], octachloronaphthalene[46] and Halowax 1031 and 1014[90]. Two examples are shown in Fig. 11a and 11b. It is worthwhile stressing that, contrary to general ideas, the odd-electron ions are always more intense than neighbouring even-electron ions. This phenomenon, together with the highly characteristic $^{35}Cl/^{37}Cl$ isotope distribution, considerably facilitates the recognition of (poly)chloroaromatic compounds. A conveniently readable bar chart of the isotopic abundance ratios for 1–15 chlorine atoms was presented by Hutzinger *et al.*[46]. Calculations[91] on the theoretical probability of the occurrence of ions of different masses in the molecular ion cluster for from mono- to octachloronaphthalenes are summarized in Table 14. The identification of a pentachloronaphthalene in a pesticide–Halowax 1014 mixture by means of mass spectrometry has been reported by Bonelli[92].

A detailed study has been made[44] of the mass spectra of octa- and heptachloro-

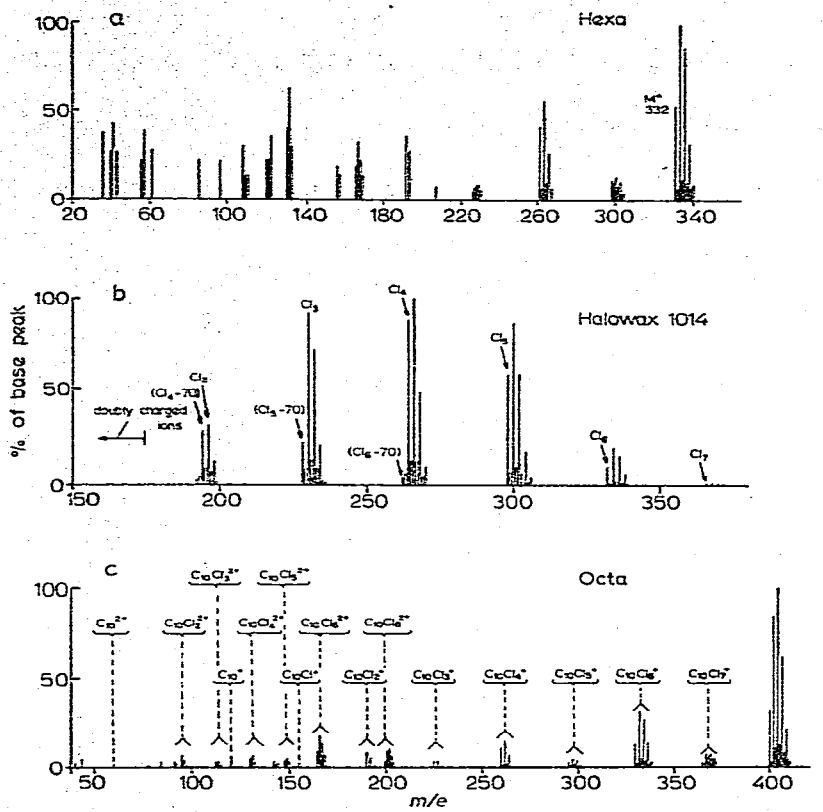


Fig. 11. Mass spectra of (a) a hexachloronaphthalene[65], (b) Halowax 1014[50] and (c) octachloronaphthalene[44]. The last spectrum was recorded at 8 kV, 70 eV on an AEI MS 902S spectrometer.

naphthalenes. With the former compound, the molecular ion can be seen (Fig. 11c) to be the base peak and the only important mode of fragmentation is by successive loss of chlorine atoms. To a large extent, the atoms are lost singly, but some simultaneous loss of two chlorine atoms may also occur. Moreover, all eight chlorine atoms may be shed successively without loss of a carbon atom, as indicated by the peaks for the series of $C_{10}Cl_8^+$–C_{10}^+ ions. In addition to the series of singly charged ions, a corresponding series of doubly charged ions occurs. The general abundance of odd-electron ions such as M^+ and $[M - Cl_2]^+$ has already been noted above. Interpretation of the spectra of the heptachloronaphthalenes, which are indistinguishable except for minor differences in the relative intensities of some of the peaks, is in accord with that of the mass spectrum of octachloronaphthalene. Again, the major mode of fragmentation is by successive loss of (all seven) chlorine atoms, the odd-electron ions are most abundant and doubly charged versions of all of the ions are apparent. Loss of chlorine is strongly preferred to loss of the hydrogen atom, which does not occur to an appreciable extent until at least four chlorine atoms have been shed.

Lastly, it is interesting to note the presence of a group of low-intensity peaks due to $C_{10}HCl_7^+$ ions in the mass spectrum recorded in Fig. 11c. Clark *et al.*[44] produced evidence that suggests that these ions are due mainly to slow incorporation of

TABLE 14

THEORETICAL PROBABILITY OF THE OCCURRENCE OF IONS IN THE MOLECULAR CLUSTER OF PCNs[60]

Values expressed relative to the most intense ion in the cluster; parent ion always lowest *m/e* in the group.

m/e	*Theoretical probability*	*m/e*	*Theoretical probability*	*m/e*	*Theoretical probability*	*m/e*	*Theoretical probability*
Mono-PCN		*Tetra-PCN*		*Hexa-PCN*			
162	100.00	264	76.35	332	50.98	375	1.95
163	11.28	265	8.61	333	5.75	376	3.48
164	33.17	266	100.00	334	100.00	377	0.38
165	3.68	267	11.23	335	11.24	378	0.39
		268	49.25	336	81.83		
Di-PCN		269	5.49	337	9.16	*Octa-PCN*	
196	100.00	270	10.86	338	35.79	400	33.44
197	11.28	271	1.19	339	3.98	401	3.77
198	65.77	272	0.92	340	8.84	402	87.40
199	7.35			341	0.97	403	9.83
200	11.00	*Penta-PCN*		342	1.17	404	100.00
201	1.20	298	61.14			405	11.22
		299	6.89	*Hepta-PCN*		406	65.44
Tri-PCN		300	100.00	366	43.71	407	7.31
230	100.00	301	11.24	367	4.93	408	26.81
231	11.27	302	65.54	368	100.00	409	2.98
232	98.37	303	7.33	369	11.25	410	7.05
233	11.03	304	21.55	370	98.12	411	0.78
234	32.44	305	2.39	371	11.00	412	1.16
235	3.59	306	3.57	372	53.56	413	0.13
236	3.65	307	0.39	373	5.98		
237	0.39	308	0.24	374	17.58		

hydrogen atoms by thermal reaction on the surface of the inlet system and source of the mass spectrometer. This indicates that the spectra of labile polychloroaromatic compounds must be interpreted with care, especially if the compounds are present in low concentrations and are introduced other than on a direct insertion probe. As another limitation of mass spectrometry for the analysis of polychloro compounds, Clark *et al.* mentioned the fact that these compounds are often very difficult to remove from the source of the spectrometer and affect subsequent spectra for many hours.

5. Electrochemistry

Farwell *et al.*[75,93] studied the use of voltammetry for the identification of PCNs and other polychlorinated compounds. Polyhaloaromatics are known to be irreversibly reduced at a mercury electrode, usually in a stepwise manner, the voltammetric reduction potentials of the various C–Cl bonds depending upon the structural positions in the parent molecule. In order to improve significantly the quantitative resolution of the individual peaks, Farwell *et al.* used interrupted-sweep voltammetry instead of normal voltammetry. They described[75] an inexpensive interrupted-sweep instrument that permits the resolution of reduction peaks separated by less than 60 mV, while it has a potential resolution of 43 mV for overlapping reduction peaks. Illustrative

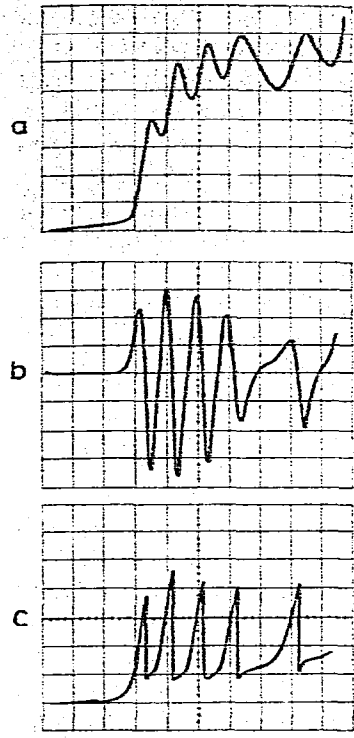


Fig. 12. Voltammograms of 1,2,3,4-tetrachloronaphthalene[75]. Voltage range: −0.700 to −2.600 V *vs.* S.C.E. (a) Normal scan; (b), second-derivative scan; (c), interrupted-sweep fingerprint.

voltammograms of 1,2,3,4-tetrachloronaphthalene are shown in Fig. 12. The most cathodic peak corresponds to the reduction of naphthalene and the remaining peaks represent the stepwise removal of the chlorine atoms.

Characteristic reduction-potential data for 37 PCNs are given in Table 10. The first zero-crossing of the second derivative of the cell current has been chosen as the interrupt potential E_{2d} on the reduction wave, as it is readily determined experimentally and is sufficiently anodic relative to the peak potential to provide good resolution between waves. Fairly large day-to-day variations in the reproducibility of the E_{2d} data have occasionally been observed. However, each reduction peak varies by the same magnitude; *i.e.*, the ΔE_{2d} values are constant. Further, all of the voltammograms contain the reduction peak for naphthalene ($E_{2d} = -2.326$ V *vs.* S.C.E.), which can be used as an internal standard.

Using the equipment described, the fingerprint technique requires at least 9 μg of relatively pure compound in order to obtain positive identification. That is, the components of a complex mixture must be separated by a chromatographic technique before they can be identified.

6. Photochemistry

In recent years, increasing attention has been paid to the photochemistry of chlorinated compounds such as organochlorine pesticides, PCBs and, to a lesser extent,

PCNs. In view of the high chemical stability of these compounds, environmental breakdown initiated by the photochemically active part of the solar spectrum is of particular interest*. Photodegradation of the pollutants may lead to their removal from the environment, *e.g.*, through conversion into insoluble polymeric material, or to the formation of much less or, alternatively, more highly toxic products. It is known that halogenoaromatic compounds chiefly undergo reductive dechlorination, dimerization and substitution by the solvent; however, chlorination and, possibly, isomerization may also occur. In this section, the limited amount of information available on the photodegradation of PCNs is discussed in more detail.

In the photolysis of 1-monochloronaphthalene in a mixture of *n*-hexane and ethanol, Szychlinski[95] observed Cl^- formation, which increased when the proportion of ethanol in the mixture was increased. Robinson and Vernon[96] reported that in ethanol, 1-monochloronaphthalene (concentration *ca.* 0.1 %) is reduced to naphthalene noticeably faster than it gives 1-phenylnaphthalene under similar conditions but in benzene. This difference is probably due to predominant absorption and inefficient sensitization by benzene at the low concentrations of substrate employed, whereas in ethanol the halogen-containing compound itself absorbs the incident light. The photolysis of 1-monochloronaphthalene ($8.5 \cdot 10^{-2}$ m*M*) in degassed solutions of 50% aqueous methanol containing potassium hydroxide has been carried out[97] using light with a wavelength of 280 ± 10 nm. Naphthalene was formed, its quantum yield increasing with increasing concentration of the base; however, the reaction also took place in neutral medium. Under the conditions employed, no formation of naphthol (quantum yield $<10^{-4}$) was observed. Replacement of a halogen by a hydrogen atom probably takes place by electron transfer from the nucleophile (OH^-) to an excited PCN molecule, and subsequent dissociation of the resulting chloroaromatic radical anion into a chlorine atom and an aromatic radical, which splits off a hydrogen atom from one of the components of the medium (however, also see below).

Ruzo *et al.*[98] carried out irradiations of 1- and 2-mono- and 1,2-dichloronaphthalene at 300 nm using methanol, cyclohexane and acetonitrile–water (4:1, v/v) as solvents. The results are summarized in Table 15. In a subsequent paper[99], the results of the photodegradation of a large series of mono- to tetrachloronaphthalenes were presented. In cyclohexane, naphthalene and binaphthyl were the major products; in methanol, however, methoxylated and more highly chlorinated naphthalenes and binaphthyls were also formed. However, no evidence was found for the isomerization of 1- to 2-monochloronaphthalene, previously claimed by Mamedov and Nasibov[100] to occur next to dechlorination. Ruzo and co-workers reported a wide range of dechlorination:dimerization ratios that indicated marked substituent effects, which are probably both electronic and steric in nature. Dechlorination is favoured with PCNs that have adjacent (*vicinal* and *peri*) chlorine atoms, while unhindered PCNs give mostly dimers; moreover, the former type of PCNs show large relative reaction rates.

The major organic products found suggest that free radical intermediates are involved; sensitization experiments in the presence of benzophenone and experiments with atmospheric oxygen indicated the occurrence of an intermediate triplet excited

* For a general discussion of the choice of conditions of irradiation, laboratory models for natural conditions, general theoretical aspects of photochemistry, etc., the reader should consult, *e.g.*, ref. 94 and ref. 9, Ch. 6.

TABLE 15

DISTRIBUTION OF PHOTOPRODUCTS AND QUANTUM YIELDS FOR REACTION OF SIMPLE HALONAPHTHALENES[98]

PCN	*Solvent*	*Φ**	*Dehalogenation***	*Binaphthyls*	*Substitution*	*Chlorination*
1	CH_3OH***	0.005	74	25		<1
1	CH_3OH–O_2	0.002	76	23		<1
1	C_6H_{12}		88	12		
1	CH_3CN–H_2O		<1	94	5	<1
2	CH_3OH***	0.007	58	38	4	
2	CH_3OH–benzophenone	0.007	2	97	1	
2	C_6H_{12}		72	28		
2	CH_3CN–H_2O		2	94	4	
1,2	CH_3OH	0.012	32	66	2	
1,2	CH_3OH–benzophenone	0.014	28	68	4	

* Degassed solutions, 20–60-h irradiations.

** Yields were estimated as percentage of total product formation by comparison with standard concentrations of naphthalene and binaphthyl.

*** The material balance on naphthyl residues was >95% in the early stages of the reaction (6 h).

state as the principal precursor of both free radical and methoxylated products. Attempts[98,101] to determine the triplet lifetimes of the PCNs by quenching experiments led to abnormal behaviour, in that enhanced quantum yields for reaction (PCN disappearance and naphthalene formation) were found with potential triplet quenchers such as 1,3-cyclohexadiene, biacetyl and *trans*-stilbene.

On the basis of the evidence, Ruzo and co-workers concluded that the major products in their studies clearly resulted from C–Cl bond fission, which, however, is more likely to involve electron transfer:

$$\mathrm{ArCl} \xrightarrow{h\nu} \mathrm{ArCl}^* \xrightarrow{\mathrm{X}} \mathrm{Ar}\cdot + \mathrm{Cl}^- \qquad (3)$$

rather than direct homolytic fission:

$$\mathrm{ArCl} \xrightarrow{h\nu} \mathrm{ArCl}^* \longrightarrow \mathrm{Ar}\cdot + \mathrm{Cl}\cdot \qquad (4)$$

This postulate is supported by the fact that the quantum yield for the disappearance of 1-monochloronaphthalene increases 8-fold in the presence of triethylamine, a known electron donor. Subsequently, the aryl radical either abstracts a hydrogen atom from a solvent molecule or attacks a molecule of starting material to form a dechlorinated product and a binaphthyl, respectively. Recently, it has been suggested[94,98] that in dimerization and substitution reactions, an aryl radical cation rather than an aryl radical reacts with a substrate or solvent molecule.

In aqueous acetonitrile[98], which can be considered to be a good model system for environmental photochemistry, the main photoproducts from monochloronaphthalene are chlorobinaphthyl, 1-naphthol and a hydroxylated dimer. In the presence of oxygen, the dimers are largely suppressed and 1-naphthol is the major product. A typical reaction scheme[94] for the photolysis of a polychloronaphthalene in an aqueous system is shown in Fig. 13.

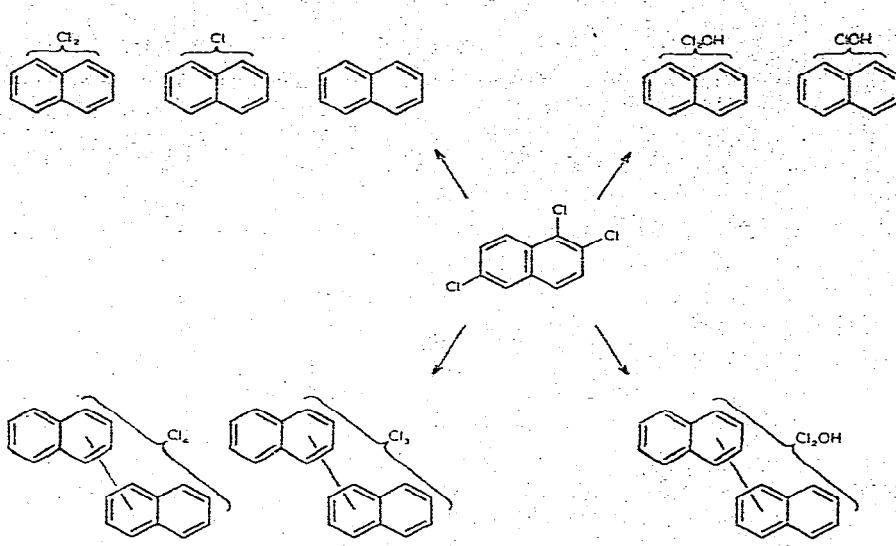


Fig. 13. Photolysis (at 300 nm) of 1,2,6-trichloronaphthalene in an aqueous medium[94]. Dechlorination, substitution and dimerization reactions are seen to occur.

Lastly, irradiation with sunlight[99] of Halowax 1014 and 2-mono- and 1,5-dichloronaphthalene as solid films on quartz produces only insoluble polymeric material. In view of the facile generation of radicals in solution photochemistry, this result is not surprising.

IV. TOXICITY AND METABOLISM

1. Toxicity

PCNs (and many other types of chloroaromatic compounds) have been implicated in various diseases, such as chloracne, X-disease in cattle and chicken oedema. Therefore, in studies on the toxicity of such compounds, *e.g.*, chlorinated naphthalenes, one should always be aware of the role possibly played by small amounts of highly toxic contaminants, such as chlorinated dibenzodioxins and dibenzofurans, for example.

(a) Chloracne[12,102]

The symptoms of this disease, which derives its name from the fact that early workers blamed nascent chlorine for its occurrence, are the formation of comedones with or without cysts and pustules[12]. The follicular orifices are filled with sebaceous and keratinous material, and melanosis and a secondary inflammatory reaction may exist. In some cases aetheroma, pigmentation and photodermatitis have been observed[103]. Chloracne is one of the most frequent forms of occupational dermatitis, and many cases due to PCNs have been reported (*e.g.*, refs. 103–126). The use of chlorinated naphthalenes as substitutes for natural waxes and rubber in Germany during World War I led to the first large outbreaks of chloracne. Massive outbreaks also occurred in the late 1930s and 1940s, chiefly in the manufacture and use of electrical cables whose covering was a fabric impregnated with penta- and hexachloronaphthalenes.

There is little doubt[102] that most cases in industry were due to external contact with PCNs alone, especially when only one side of the body was involved. However, it has been proved conclusively that chloracne can also result from systemic intoxication of the human subject with no external contact. Fumes of PCNs are by far the most potent, solutions less so, and contact with the solid substance is of little importance except under special conditions, such as when friction also occurs[127]. Even more important is the degree of chlorination of the PCNs. Contrary to the ideas of early workers that as the degree of chlorination increases so do the systemic toxicity and acneigenic properties, studies by Shelley and Kligman[128], Hambrick[123] and Crow[102] (and the large outbreaks of acne around 1940) have shown unequivocally that whereas mono-, di-, tri-, tetra-, hepta- and octachloronaphthalenes are entirely non-acneigenic, the penta- and hexachloro derivatives (Halowax 1014) produce very severe chloracne. In refs. 123 and 128, and also in a paper by Plewig[125], details can be found concerning the experimental production of acne in male adults, the PCNs being acneigenic in man in every area of the body tested.

(b) Liver damage

The disease occurs independently from chloracne[115], and usually manifests itself after an exposure of 4–6 months, but may occur in as short a time as 7 weeks. Occasionally loss of appetite, nausea and oedema of the face and hands are the first symptoms. Abdominal pain and vomiting follow, and then jaundice develops[12,129]. Flinn and Jarvik[130] reported nine cases with a fatal outcome following exposure to PCNs; at autopsy, yellow atrophy of the liver was found. Further reports of liver damage in human subjects are given in refs. 112–114 and 131–136. In rats, guinea-pigs and other test animals, acute yellow atrophy and other liver changes have been observed[12,130–132,137–141] in feeding and inhalation experiments. For example, upon feeding hexachloronaphthalene to rats, Schoettle *et al.*[141] observed mild to moderate fatty degeneration of the liver with centrilobular vacuolation of the hepatic cells. Oral administration of pentachloronaphthalene to guinea-pigs caused fat degeneration of the liver, loss of weight, conjunctivitis and death[122]. Lastly, degenerative lesions of the liver and kidneys occurred[142] in young swine fed with hexachloronaphthalenes, while necrosis and cirrhosis of the liver have been observed in sheep after ingestion of feed containing highly chlorinated naphthalenes[143]. From the above results, one can conclude that PCNs with high chlorine contents produce liver damage in several species. In man, effects such as leucopenia, lymphopenia, reduced amounts of haemoglobin and glucose in the blood and hyperacidic gastritis have also been observed[124].

(c) X-disease

In the U.S.A. in 1941, the term X-disease was applied to a cattle disease of unknown etiology. After further outbreaks in 1942–1946, Olafson described[144] the disease in 1947 and, a few years later, produced evidence[145,146] to show that it is caused by highly chlorinated naphthalenes[147].

The symptoms of poisoning include complete weakness, draggy loop, excessive lacrimation, night-blindness, diarrhoea, polyuria, marked salivation and discharge from the nostrils[12,148]. Cattle show a rapid decline in vitamin A plasma levels[148,149]. A chronic cough, poor appetite and numerous red maculae in the buccal mucosa develop

and hyperkeratosis of the skin follows. Degeneration of cells in the pancreas and liver and gall-bladder and renal-cortex damage have also been observed[12,150]. In a study on the ability of various PCNs to cause X-disease, Bell[151] reported that di- and trichloro derivatives do not produce the disease in calves, tetrachloronaphthalenes have an effect and the highly (penta- to octa-)chlorinated naphthalenes cause severe disease. However, octachloronaphthalene is less toxic than hexa- and heptachloro derivatives. Similar results have been obtained in various other studies[147,152–157]. Vlachos and co-workers[158,159] reported a rapid decrease in the semen quality of a bull following feeding of highly chlorinated naphthalenes. The first change observed was a decrease in mobility of the sperms and a marked increase in the proximal protoplastic droplets; spermatogenesis then stopped. Cats, dogs, rats and chickens, impregnated or fed with PCNs with a high chlorine content, suffer[141,160,161] typical symptoms of X-disease, which appears after varying periods of time. No symptoms have been found after administration of PCNs with relatively low chlorine content.

Chronic periodic inhalation of chloronaphthalene vapour by rats causes a decrease in the urea level of the urine and in the blood-sugar level[140]. Other changes include an increase in the cholesterol and a decrease in the ascorbic acid concentrations in the blood. Octachloronaphthalene, when fed to rats, greatly accelerates the loss of vitamin A from the liver[162]. There is no effect on vitamin A or E in the blood, nor does vitamin E in the liver change. According to Hill and Siegmund[163], vitamin E inhibits the loss of vitamin A from the liver.

Pigs do not show the characteristic symptoms of X-disease[142], although hexachloronaphthalene produces hyperplasia of the vaginal epithelium with keratin formation and a depression of the vitamin A plasma level. According to another report[164], pigs have a much greater tolerance than cattle for PCNs. A similar conclusion was drawn by Brock *et al.*[143] when comparing sheep and cattle.

(d) Chicken oedema[12]

In 1957, a disease occurred in a large number of chickens and it was discovered that the residue of certain distilled animal fats produces the condition when they are added to the chicken diet. The disease was called chicken oedema because it manifests itself with hydropericardium and ascites in chickens. Ducks and turkeys experience a reduction in growth.

Toxic fat is not the only product capable of producing the chicken oedema syndrome. A mixture of penta- and hexachloronaphthalenes (Halowax 1014), when fed to chickens, results in chicken oedema[165]. On the other hand, Halowax 1051 has no adverse effects[166]. In a study[167,168] on the toxicity of some European PCB mixtures (Phenoclor DP6 and Clophen A60) and one from the U.S.A. (Aroclor 1260), the two European products were found to have greater toxicity and to produce centrilobular liver necrosis. Moreover, chicken oedema is a common finding, rare with Aroclor 1260. All three mixtures produced porphyria. Fractionation of the PCB mixtures over a Florisil column, followed by GLC and mass-spectrometric and microcoulometric analyses, revealed the presence of tetra- and pentachlorodibenzofurans and hexa- and heptachloronaphthalenes in the European samples but not in the Aroclor sample. In view of the known high toxicity of polychlorodibenzofurans, these compounds must be assumed largely to determine the (high) toxicity of the Phenoclor and Clophen preparations.

The interference of Halowaxes and other chloroaromatics in the TLC/GLC detection of chicken oedema factor has been studied by Huang *et al.*[169].

(e) Miscellaneous

Craigie and Hutzinger[170] compared the effects of several types of chloroaromatic compounds on marine phytoplankton. Halowax 1099, at the 100 ppm level, kills *Olisthodiscus* and strongly depresses the growth of *Thalassiosira fluviatilis*. However, it is not toxic to *Dunaliella tertiolecta*.

2. Metabolism

Cleary *et al.*[171] fed a mixture of PCNs (mainly penta- and hexachloronaphthalenes) to rats and dogs and found no significant storage of material in the lungs, skin or kidneys, nor was any significant amount excreted in the urine. Apparently, the animals are able to remove the chlorinated compounds promptly. In the dog, an increase in the urinary ethereal sulphate fraction, but no significant change in the neutral sulphur excretion, was noted after PCN feeding. Drinker[138] reported a high percentage of chloride in the urine of a dog after administration of hexachloronaphthalene.

An extensive study on the metabolism of PCNs was made by Cornish and Block[172], who administered naphthalene, 1-monochloronaphthalene and di-, tetra-, penta-, hepta- and octachloronaphthalenes to rabbits. Analysis of the urine samples for a large number of excretory products during 4 days indicated that naphthalene and mono- and dichloronaphthalene are metabolized readily. Tetrachloronaphthalene is metabolized to a lesser extent in the 4-day period, while the more highly chlorinated products do not yield urinary metabolites that could be detected by the procedure used by Cornish and Block. Possibly these compounds are metabolized by pathways that yield excretory products not included in the study, or they may be deposited in tissues and metabolized or excreted unchanged over longer periods of time. Cornish and Block suggested that a high degree of chlorination interferes with the formation of a 1,2-dihydro-1,2-diol type of compound, which has been proposed[173] as an intermediate in naphthalene metabolism.

Ruzo and co-workers[43,174,175] also studied the metabolism of PCNs. When frogs and pigs were given Halowax 1031, whose main constituents are monochloronaphthalenes (Table 1), or one of several mono-, di- and tetrachloronaphthalenes, the

TABLE 16

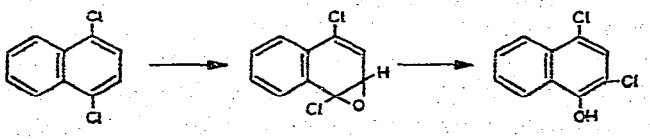
SURVEY OF PCN METABOLITES

PCN	*Metabolite*	*Animal*	*Reference*
1	4-Chloro-1-naphthol	Frog, pig	174, 175
2	3-Chloro-2-naphthol	Pig	175
1,2	3,4-Dichloro-1-naphthol	Pig	43
1,4	2,4-Dichloro-1-naphthol	Pig, frog	43, 174
1,2,3,4	5,6,7,8-Tetrachloro-1- and -2-naphthol	Pig, frog	43, 174
1,2,3,4,5,6	— *	Pig	43

* No isolatable metabolite transformation products obtained.

major metabolites were invariably phenolic products; dechlorination has not been observed with any of the PCNs investigated.

The structure of several major metabolites has been assigned on the basis of TLC, GLC and mass-spectrometric data; the results are summarized in Table 16. The mechanism of the metabolism of 1,4-dichloronaphthalene has been explained[43,174] in terms of the formation of an initial epoxidation of the naphthalene nucleus to give an arene oxide, its decomposition being accompanied by a 1,2-migration of a halogen atom:



(5)

In contrast with the lower chlorinated naphthalenes, 1,2,3,4,5,6-hexachloronaphthalene does not yield any urinary metabolites.

REFERENCES

1 A. Laurent, *Ann. Chim. Phys.*, (2), 52 (1833) 275.
2 E. Fischer, *Chem. Ber.*, 11 (1878) 735.
3 J. W. Aylsworth, *U.S. Pat.*, No. 914,222 (1909).
4 J. W. Aylsworth, *U.S. Pat.*, No. 914,223 (1909).
5 J. W. Aylsworth, *U.S. Pat.*, No. 1,111,289 (1913).
6 D. W. F. Hardie, *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 5, Interscience, New York, 2nd ed., 1964, p. 297.
7 Prodelec, Paris, personal communication.
8 F. A. Beland and R. D. Geer, *J. Chromatogr.*, 84 (1973) 59.
9 O. Hutzinger, S. Safe and V. Zitko, *The Chemistry of PCBs*, CRC press, Cleveland, Ohio, 1974, Ch. 2.
10 L. Fishbein, *J. Chromatogr.*, 68 (1972) 345.
11 J. Sherma, *Advan. Chromatogr.*, 12 (1975) 141.
12 R. D. Kimbrough, *Arch. Environ. Health*, 25 (1972) 125.
13 *Halowax® Chlorinated Naphthalene Oils and Waxlike Solids*, Technical Bulletin, Koppers Co., Pittsburgh, Pa.
14 *Nibren Wachse*, Technical Bulletin, Bayer, Leverkusen, 1970.
15 F. D. Kover, *Environmental Hazard Assessment Report —Chlorinated Naphthalenes*, EPA 560/8-75-001, 1975.
16 W. Schwemberger, *J. Gen. Chem. U.S.S.R.*, 8 (1938) 1353.
17 H. Vollmann, *Ullmanns Enzyklopädie der Technischen Chemie*, Vol. 5, Urban und Schwarzenberg, Berlin, 1956, p. 474.
18 ICI, Mond Division, Runcorn, personal communication.
19 E. G. Turner and W. P. Wynne, *J. Chem. Soc.*, (1941) 243.
20 P. S. Varma, N. B. Parekh and V. K. Subramanium, *J. Indian Chem. Soc.*, 16 (1939) 460.
21 H. Wahl and H. Basilios, *Bull. Soc. Chim. Fr.*, (1947) 482.
22 H. E. Armstrong and W. P. Wynne, *Chem. News*, 73 (1896) 55.
23 R. W. Beattie and F. C. Whitmore, *J. Amer. Chem. Soc.*, 55 (1933) 1546.
24 P. Ferrero and G. Bolliger, *Helv. Chim. Acta*, 11 (1928) 1144.
25 H. E. Armstrong, *Chem. News*, 58 (1888) 295.
26 H. E. Armstrong and W. P. Wynne, *Chem. News*, 71 (1895) 254.
27 P. T. Cleve, *Chem. Ztg.*, 17 (1893) 398.
28 H. E. Armstrong and W. P. Wynne, *Chem. News*, 61 (1890) 273.
29 H. E. Armstrong and W. P. Wynne, *Chem. News*, 59 (1889) 188.

30 H. E. Armstrong and W. P. Wynne, *Chem. News*, 76 (1897) 69.
31 L. Cencelj, *Chem. Ber.*, 93 (1960) 988.
32 A. Hardy, E. R. Ward and L. A. Day, *J. Chem. Soc.*, (1956) 1979.
33 H. A. Piggott and F. H. Slinger, *J. Chem. Soc.*, (1952) 259.
34 J. Chatt and W. P. Wynne, *J. Chem. Soc.*, (1943) 33.
35 E. Clar and Ch. Marschalk, *Bull. Soc. Chim. Fr.*, (1950) 443.
36 A. Atterberg and O. Widman, *Chem. Ber.*, 10 (1877) 1841.
37 A. Atterberg and O. Widman, *Bull. Soc. Chim. Fr.*, 28 (1877) 513.
38 H. Riemlinger and G. King, *Chem. Ber.*, 95 (1962) 1043.
39 C. Graebe, *Justus Liebigs Ann. Chem.*, 149 (1869) 1.
40 Ad. Claus and H. van de Lippe, *Chem. Ber.*, 16 (1883) 1016.
41 O. Widman, *Bull. Soc. Chim. Fr.*, 28 (1877) 505.
42 C. A. Lobry de Bruyn and F. H. van Leent, *Rec. Trav. Chim. Pays-Bas*, 15 (1896) 87.
43 L. O. Ruzo, D. Jones, S. Safe and O. Hutzinger, *J. Agr. Food Chem.*, 24 (1976) 581.
44 J. Clark, R. Maynard and B. J. Wakefield, *J. Chem. Soc. Perkin II*, (1976) 73.
45 N. A. Tahir, *M.Sc. Thesis*, Univ. Salford, 1975.
46 O. Hutzinger, S. Safe and V. Zitko, *Int. J. Environ. Anal. Chem.*, 2 (1972) 95.
47 J. P. Wibaut and G. P. Bloem, *Rec. Trav. Chim. Pays-Bas*, 69 (1950) 586.
48 R. Stroh, *Houben-Weyl*, Vol. 5, Thieme, Stuttgart, 1962, p. 669.
49 A. Weissberger, R. Sängewald and G. C. Hampson, *Trans. Faraday Soc.*, 30 (1934) 884.
50 *Beilstein*, Band V, Springer-Verlag, Berlin, 1944, System No. 475–480.
51 *Elseviers Encyclopedia of Organic Chemistry*, Vol. 12B, Elsevier, Amsterdam, 1948.
52 W. P. Wynne, personal communication in ref. 51.
53 G. Ruoff, *Chem. Ber.*, 9 (1876) 1483.
54 W. Schwemberger and W. Gordon, *J. Gen. Chem. U.S.S.R.*, 2 (1932) 921.
55 H. Brintzinger and H. Orth, *Monatsh. Chem.*, 85 (1954) 1015.
56 H. Suschitzky, *Polychloroaromatic Compounds*, Plenum Press, London, New York, 1975.
57 M. Ballester, J. Castañer and J. Riera, *Clearinghouse Fed. Sci. Tech. Inform.*, 1968, AD 672319.
58 J. Goubeau, H. Luther, K. Feldmann and G. Brandes, *Chem. Ber.*, 86 (1953) 214.
59 H. Luther, G. Brandes, H. Günzler and B. Hampel, *Z. Elektrochem.*, 59 (1955) 1012.
60 H. de Laszlo, *J. Amer. Chem. Soc.*, 50 (1928) 892.
61 L. Greenburg, *Ind. Med. Surg.*, 12 (1943) 520.
62 J. A. Armour and J. A. Burke, *J. Ass. Offic. Anal. Chem.*, 54 (1971) 175.
63 *Pesticide Analytical Manual*, Vol. 1, Food and Drug Administration, Washington, D.C., 1969.
64 J. A. Armour and J. A. Burke, *J. Ass. Offic. Anal. Chem.*, 53 (1970) 761.
65 D. F. Goerlitz and L. M. Law, *Bull. Environ. Contam. Toxicol.*, 7 (1972) 243.
66 A. V. Holden and K. Marsden, *J. Chromatogr.*, 44 (1969) 481.
67 V. Zitko, *Int. J. Environ. Anal. Chem.*, 1 (1972) 221.
68 M. P. Gulan, D. D. Bills and T. B. Putnam, *Bull. Environ. Contam. Toxicol.*, 11 (1974) 438.
69 D. L. Stalling and J. N. Huckins, *J. Ass. Offic. Anal. Chem.*, 56 (1973) 367.
70 U. A. Th. Brinkman, A. de Kok, H. G. M. Reymer and G. de Vries, *J. Chromatogr.*, 129 (1976) 193.
71 S. B. Challen and M. Kučera, *J. Chromatogr.*, 31 (1967) 345.
72 L. Cencelj and D. Hadži, *Spectrochim. Acta*, 7 (1955) 274.
73 U. A. Th. Brinkman, J. W. F. L. Seetz and H. G. M. Reymer, *J. Chromatogr.*, 116 (1976) 353.
74 U. A. Th. Brinkman, A. de Kok and I. P. Meulenberg, in preparation.
75 S. O. Farwell, F. A. Beland and R. D. Geer, *Anal. Chem.*, 47 (1975) 895.
76 J. Ferguson and R. L. Werner, *J. Chem. Soc.*, (1954) 3645.
77 G. O. Kalmykova, N. D. Kurmei and N. N. Malykhina, *Izv. Akad. Nauk S.S.S.R., Ser. Fiz.*, 39 (1975) 1925.
78 U. A. Th. Brinkman and A. de Kok, *J. Chromatogr.*, 129 (1976) 451.
79 D. C. Holmes and M. Wallen, *J. Chromatogr.*, 71 (1972) 562.
80 W. Müller, H. Rohleder, W. Klein and F. Korte, *GSF-Bericht Ö 104*, München, 1974.
81 D. T. Williams and B. J. Blanchfield, *J. Ass. Offic. Anal. Chem.*, 55 (1972) 93.
82 U. A. Th. Brinkman, in preparation.
83 O. Hutzinger, W. D. Jamieson, S. Safe and V. Zitko, *J. Ass. Offic. Anal. Chem.*, 56 (1973) 982.
84 B. Zimmerli, *J. Chromatogr.*, 88 (1974) 65.

85 W. L. Mosby, *J. Amer. Chem. Soc.*, 77 (1955) 759.
86 H. W. Thompson, *J. Chem. Soc.*, (1948) 329.
87 L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen, London, p. 64.
88 S. Safe and O. Hutzinger, *Chem. Commun.*, (1972) 260.
89 S. Safe, O. Hutzinger and W. D. Jamieson, *Org. Mass Spectrom.*, 7 (1973) 169.
90 S. Safe and O. Hutzinger, *Mass Spectrometry of Pesticides and Pollutants*, CRC Press, Cleveland, Ohio, 1973, Ch. 5.
91 J. W. Rote and W. J. Morris, *J. Ass. Offic. Anal. Chem.*, 56 (1973) 188.
92 E. J. Bonelli, *Anal. Chem.*, 44 (1972) 603.
93 S. O. Farwell, F. A. Beland and R. D. Geer, *Bull. Environ. Contam. Toxicol.*, 10 (1973) 157.
94 L. O. Ruzo, G. Sundström, S. Safe and O. Hutzinger, *Chem. Weekbl.*, 35 (1976) m 422.
95 J. Szychlinski, *Rocz. Chem.*, 34 (1960) 941.
96 G. E. Robinson and J. M. Vernon, *J. Chem. Soc., C*, (1971) 3363.
97 Yu. Yu. Kulis, I. Yu. Poletaeva and N. G. Kuz'min, *J. Org. Chem. U.S.S.R.*, 9 (1973) 1242.
98 L. O. Ruzo, N. J. Bunce and S. Safe, *Can. J. Chem.*, 53 (1975) 688.
99 L. O. Ruzo, N. J. Bunce, S. Safe and O. Hutzinger, *Bull. Environ. Contam. Toxicol.*, 14 (1975) 341.
100 K. I. Mamedov and I. K. Nasibov, *Zh. Prikl. Spektrosk.*, 11 (1969) 859.
101 L. O. Ruzo and N. J. Bunce, *Tetrahedron Lett.*, 8 (1975) 511.
102 K. D. Crow, *Trans. St. John's Hosp. Dermatol. Soc.*, 56 (1970) 79.
103 S. Nomura, *Rept. Inst. Sci. Labor., Tokyo*, 47 (1953) 21.
104 V. Waver, *Z. Gewerbehyg.*, 6 (1918) 100.
105 Wm. B. Fulton and J. L. Matthews, *Pa. Dep. Labor Ind. Spec. Bull.*, 43 (1936) 15.
106 H. Haldin-Davis, *Brit. J. Dermatol. Syph.*, 51 (1939) 380.
107 A. Thellwell Jones, *J. Ind. Hyg. Toxicol.*, 23 (1941) 290.
108 M. R. Mayers and M. C. Silverberg, *J. Ind. Hyg. Toxicol.*, 20 (1938) 244.
109 L. Greenburg, *Ind. Med. Surg.*, 12 (1943) 520.
110 G. E. Morris and I. R. Tabershaw, *J. Amer. Med. Ass.*, 121 (1943) 192.
111 E. F. Kelbey, *Urol. Cutaneous Rev.*, 47 (1943) 238.
112 L. Greenburg, *Ind. Bull. N.Y. State Dep. Labor*, 22 (1943) 404.
113 E. Collier, *Lancet*, 244 (1943) 72.
114 H. von Wedel, W. A. Holla and J. Denton, *Rubb. Age*, 53 (1943) 419.
115 L. Teleky, *Klin. Wochenschr.*, 27 (1949) 249.
116 V. M. Gavrilova, *Vestn. Venerol. Dermatol.*, (1949) 32.
117 S. Nomura, *J. Sci. Lab.*, 29 (1953) 57.
118 J. Roubal and F. Pokorný, *Prac. Lék.*, 5 (1953) 5.
119 L. Jipísek and Z. Šťáva, *Prakt. Lék.*, 35 (1955) 34.
120 L. Angelucci and P. Gallo, *Ist. Patol. Libro Alfonso Gallo*, 13 (1954) 93.
121 W. F. von Oettingen, *Public Health Service*, 1955, publ. 414.
122 H. Bentz and I. Herdmann, *Arch. Exp. Vet.*, 10 (1956) 50.
123 G. W. Hambrick, *J. Invest. Dermatol.*, 28 (1957) 89.
124 E. A. Kapkaev, *Gig. Sanit.*, 22 (1957) 79.
125 G. Plewig, *Arch. Klin. Exp. Dermatol.*, 238 (1970) 228.
126 E. de la Vega, *Rep. N.Y. State Vet. Coll. Cornell Univ., 1957–58*, (1959) 33.
127 W. Höfs, *Dermatol. Wochenschr.*, 135 (1957) 1.
128 W. A. Shelley and A. M. Kligman, *Arch. Dermatol.*, 75 (1957) 689.
129 M. R. Mayers and A. Ross Smith, *Ind. Bull. N.Y. State Dep. Labor*, 21 (1942) 30
130 F. B. Flinn and N. E. Jarvik, *Amer. J. Hyg.*, 27 (1938) 19.
131 F. B. Flinn and N. E. Jarvik, *Proc. Soc. Exp. Biol. Med.*, 35 (1936) 118.
132 C. K. Drinker, M. F. Warren and G. A. Bennett, *J. Ind. Hyg. Toxicol.*, 19 (1937) 283.
133 L. Greenburg, M. R. Mayers and A. Ross Smith, *J. Ind. Hyg. Toxicol.*, 21 (1939) 29.
134 N. G. R. McLetchie and D. Robertson, *Brit. Med. J.*, I (1942) 691.
135 L. H. Cotter, *J. Amer. Med. Ass.*, 125 (1944) 273.
136 N. Strauss, *Rev. Gastroenterol.*, 11 (1944) 381.
137 G. A. Bennett, C. K. Drinker and M. F. Warren, *J. Ind. Hyg. Toxicol.*, 20 (1938) 97.
138 C. K. Drinker, *J. Ind. Hyg. Toxicol.*, 21 (1939) 29.
139 F. B. Flinn, *Arch. Mal. Profes.*, 2 (1939) 433.

140 N. Brodele, *Latv. PSR Zināt Akad. Vestis.*, 9 (1953) 81.
141 C. E. Schoettle, E. F. Reber, C. C. Morrill and R. P. Link, *Amer. J. Vet. Res.*, 16 (1955) 183.
142 W. G. Huber and R. P. Link, *Toxicol. Appl. Pharmacol.*, 4 (1962) 257.
143 W. E. Brock, E. W. Jones, R. MacVicar and L. S. Pope, *J. Vet. Res.*, 8 (1957) 625.
144 P. Olafson, *Cornell Vet.*, 37 (1947) 279.
145 W. Hansel, P. Olafson and K. McEntee, *Cornell Vet.*, 45 (1955) 94.
146 P. Olafson, W. Hansel and K. McEntee, *Rep. N.Y. State Vet. Coll. Cornell Univ., 1953–54*, (1954) 54.
147 R. Ferrando, *Bull. Soc. Chim. Biol.*, 36 (1954) 1245.
148 D. J. Welsh, *Amer. J. Med. Technol.*, 23 (1957) 43.
149 C. L. Marsh, C. Olson, Jr. and I. C. Blore, *Amer. J. Vet. Res.*, 17 (1956) 410.
150 D. Sikes and M. E. Bridges, *Science*, 116 (1952) 506.
151 W. B. Bell, *Vet. Med.*, 48 (1953) 135, 146.
152 D. Sikes, J. C. Wise and M. E. Bridges, *J. Amer. Vet. Med. Ass.*, 121 (1952) 337.
153 J. S. Copenhaver and W. B. Bell, *Vet. Med.*, 49 (1953) 96.
154 P. Olafson, K. McEntee and W. Hansel, *Rep. N.Y. State Vet. Coll. Cornell Univ., 1952–53*, (1954) 58.
155 R. P. Gregory, Jr., J. C. Wise and D. Sikes, *J. Amer. Vet. Med. Ass.*, 125 (1954) 244.
156 J. Beer, *Arch. Exp. Vet.*, 10 (1956) 58.
157 K. Dedić, L. F. Müller, K. Reichel and H. Bentz, *Arch. Exp. Vet.*, 10 (1956) 87.
158 K. Vlachos and K. McEntee, *Rep. N.Y. State Vet. Coll. Cornell Univ., 1952–53*, (1954) 29.
159 K. Vlachos, K. McEntee, P. Olafson and W. Hansel, *Rep. N.Y. State Vet. Coll. Cornell Univ., 1954–55*, (1956) 25.
160 H. Köhler, *Arch. Exp. Vet.*, 8 (1954) 163.
161 H. Köhler, *Arch. Tierernähr., Beihefte*, 5 (1953) 283.
162 R. E. Diedrick, J. G. Bieri and R. R. Cardenas, Jr., *J. Nutr.*, 57 (1955) 287.
163 H. Hill and K. H. Siegmund, *Deut. Tierärztl. Wochschr. Tierärtzl. Rundsch.*, 64 (1957) 304.
164 R. P. Link, J. C. Smith and D. I. Newton, *J. Amer. Vet. Med. Ass.*, 133 (1958) 83.
165 W. J. Pudelkiewicz, R. V. Boucher, E. W. Callenbach and R. C. Miller, *Poultry Sci.*, 38 (1959) 424.
166 W. J. Pudelkiewicz, R. V. Boucher, E. W. Callenbach and R. C. Miller, *Poultry Sci.*, 37 (1958) 185.
167 J. G. Vos, J. H. Koeman, H. L. van der Maas, M. C. ten Noever de Brauw and R. H. de Vos, *Food Cosmet. Toxicol.*, 8 (1970) 625.
168 J. G. Vos and J. H. Koeman, *Toxicol. Appl. Pharmacol.*, 17 (1970) 656.
169 A. Huang, D. Firestone and A. D. Campbell, *J. Ass. Offic. Anal. Chem.*, 50 (1967) 16.
170 J. S. Craigie and O. Hutzinger, *Chemosphere*, 3 (1975) 139.
171 R. V. Cleary, J. Maier and G. H. Hitchings, *J. Biol. Chem.*, 127 (1939) 403.
172 H. H. Cornish and W. D. Block, *J. Biol. Chem.*, 231 (1958) 583.
173 E. D. S. Corner and L. Young, *Biochem. J.*, 61 (1955) 132.
174 G. Sundström, O. Hutzinger, S. Safe, L. O. Ruzo and D. Jones, in J. H. Koeman and J. J. T. W. A. Strik (Editors), *Sublethal Effects of Toxic Chemicals on Aquatic Animals*, Elsevier, Amsterdam, 1975, p. 177.
175 L. O. Ruzo, S. Safe, O. Hutzinger, N. Platonow and D. Jones, *Chemosphere*, 3 (1975) 121.
176 B. Bush and F.-C. Lo, *J. Chromatogr.*, 77 (1973) 377.