

CHROM. 10,571

DISCRIMINATION BETWEEN POLYCHLORINATED NAPHTHALENES AND POLYCHLORINATED BIPHENYLS

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(Received September 2nd, 1977)

SUMMARY

Procedures for the discrimination between polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) taken from the literature are discussed. It is demonstrated that the analysis of mixtures of PCBs and PCNs can conveniently be accomplished by both high-performance liquid and gas chromatography, after their conversion into the fully chlorinated end-products, *viz.*, decachlorobiphenyl and octachloronaphthalene, respectively. Successful analyses of Halowax 1051, which is a mixture of octa- and heptachloronaphthalenes, are also reported.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are widespread and persistent industrial pollutants of the environment that have been available commercially for over 40 years. However, the discovery of PCBs in environmental samples and the knowledge that common organochlorine pesticides and PCBs are not well separated under ordinary gas chromatographic (GC) conditions stem from 1966 only¹. Polychlorinated naphthalenes (PCNs) are manufactured for uses analogous to those of PCBs, and the physical and chemical properties of PCNs and PCBs are very similar. The separation and discrimination of organochlorine pesticides, PCBs and PCNs from each other is therefore of major interest.

Over the years, it has been shown²⁻⁵ that clean-up over an aluminium oxide-silica gel, a silica gel-Celite or an activated silica gel column may separate PCBs and PCNs from the common organochlorine pesticides. Separation by two-dimensional thin-layer chromatography has also been recommended⁶. However, in all of these instances, the degree of separation between the PCBs, or PCNs, and at least one of the pesticides, usually *p,p'*-DDE, is very small or even zero. Moreover, careful control of the activity of the adsorbent, the activation procedures and the quality of the solvents used for elution has been shown^{7,8} to be indispensable in order to obtain reproducible chromatographic conditions. Obviously, alternative procedures such as that involving chromium trioxide oxidation of *p,p'*-DDE to 4,4'-dichlorobenzophenone⁹ and perchlorination are well worth trying. In the latter approach, the separation problem is eliminated by fully chlorinating all PCBs and/or PCNs to yield

decachlorobiphenyl (DCB) and/or octachloronaphthalene (OCN). During this step, the organochlorine pesticides are converted into largely unknown end-products. Fortunately, in GC, none of these products yield peaks that coincide with those of DCB or OCN.

We can summarize the present position by stating that a skilled and experienced worker can achieve a satisfactory separation of organochlorine pesticides from PCBs and PCNs. However, no method has yet been reported for the differential elution of PCNs and PCBs. In this paper, several promising procedures taken from the literature for the discrimination between these two classes of compounds are discussed, and are compared with recent findings from this laboratory.

MATERIALS AND METHODS

Decachlorobiphenyl was purchased from Aldrich Europe (Beers, Belgium) and octachloronaphthalene was from Analabs (North Haven, Conn., U.S.A.). Halowax 1051 (Koppers, Pittsburgh, Pa., U.S.A.) is a mixture of polychlorinated naphthalenes, consisting of 80–90% octa- and 20–10% heptachloronaphthalenes. Small samples of 1H- and 2H-heptachloronaphthalene were kindly provided by Dr. B. J. Wakefield (University of Salford, Salford, Great Britain). All other chemicals were of normal analytical-grade quality.

Liquid chromatography was carried out on a Siemens S 100 chromatograph equipped with a Zeiss PM2 DLC UV detector (Siemens, Munich, G.F.R.), and on a chromatograph assembled from commercial and home-made parts, the principal ones being an Orlita 7W1515 reciprocating pump (Orlita, Giessen, G.F.R.), a manual fixed-volume (10 μ l) sample valve (Siemens) and a Schoeffel SF770 variable-wavelength double-beam spectrophotometer (Schoeffel, Westwood, N.J., U.S.A.).

The chromatographic columns were stainless-steel tubes, 25 cm \times 3 mm I.D., pre-packed with 7- μ m LiChrosorb RP-8 (Hibar; Merck, Darmstadt, G.F.R.) or 5- μ m LiChrosorb Alox T5 (Chrompack, Middelburg, The Netherlands). *n*-Hexane used as eluent was dried over molecular sieve 5A.

Gas chromatograms were run on an HP 5710A gas chromatograph (Hewlett-Packard, Avondale, Pa., U.S.A.) or a Pye Unicam GCV chromatograph (Pye, Cambridge, Great Britain), which were equipped with a flame-ionization and an electron-capture detector. Glass columns were used packed with 4% OV-101 or 1% SE-30 on Chromosorb W (HP) (80–100 mesh) or 3% OV-1 or 4% OV-17 on Chromosorb W (AW DMCS HP) (80–100 mesh).

RESULTS AND DISCUSSION

Discrimination between PCBs and PCNs

A convenient method for differentiating between PCNs and PCBs is based on the relative ease of oxidation of the former compounds as opposed to the resistance to oxidation of the latter. Holmes and Wallen¹⁰ recommended treatment of a PCN-PCB sample with an excess of chromium trioxide. After a 20-min reaction time at *ca.* 100°, examination of a suitably prepared *n*-hexane extract by GC with electron-capture detection reveals the presence of peaks due to PCBs only, the PCNs having been oxidized completely. As Holmes and Wallen only studied the behaviour of a

mixture of highly chlorinated biphenyls (Aroclor 1254), it seems useful to add that according to a later paper¹¹ treatment of PCBs with chromium trioxide-sulphuric acid leads to considerable decomposition of several low-chlorinated isomers, although no loss occurs with the more highly chlorinated biphenyls.

The analysis of a heterogeneous mixture of PCBs, PCNs and similar compounds can be simplified by converting them into a single derivative, mainly by perchlorination and dechlorination. Quantitative conversion of PCBs into DCB is effected¹² by means of, *e.g.*, antimony(V) chloride, mixtures of antimony(V) chloride and iodine and/or sulphuryl chloride, or a mixture of disulphur dichloride, sulphuryl chloride and aluminium chloride. The latter mixture and sulphuryl chloride-antimony(V) chloride (9:1, v/v) have also been recommended¹² for the perchlorination of PCNs; however, as yet no accurate data on the percentage recovery of OCN have been published.

Since the end-products are highly chlorinated, perchlorination is usually combined with electron-capture GC. Unfortunately, under the conditions normally employed in published work^{12,13} DCB and OCN have approximately the same retention times. However, according to our experiences, DCB shows distinctly stronger retention than does OCN on, *e.g.*, 4% OV-101, 3% OV-1 or 1% SE-30 on Chromosorb W at 260, 250 and 220°, respectively (Table I and Fig. 1a). With SE-30 as the stationary phase, a resolution of 1.0 is still observed if the temperature of the column is increased to 250°. At a carrier gas flow-rate of 30 ml·min⁻¹, the uncorrected retention times of OCN and DCB are only 2.76 and 3.18 min, respectively. The ratio of the molar responses of DCB and OCN to the flame-ionization and electron-capture detector is 1.25 ± 0.1 and 1.5 ± 0.1, respectively.

TABLE I

GC AND HPLC RETENTION TIMES AND UV SPECTRAL DATA FOR DCB AND OCN
GC: carrier gas, N₂ or He; flow-rate, 30 ml·min⁻¹ (SE-30, OV-101) or 27 ml·min⁻¹ (OV-1); column, 2.2 m (OV-101), 1.95 m (SE-30) or 1.8 m (OV-1), 2 mm I.D. HPLC: see legends to Figs. 1b and 1c.

Compound	<i>t</i> _{ret.} in HPLC		<i>t</i> _{ret.} in GC			Relative response (GC) to		$\epsilon \cdot 10^{-3}$ (HPLC) at	
	RP-8	Alox T	1% SE-30 (220°)	3% OV-1 (250°)	4% OV-101 (260°)	ECD	FID	215 nm	275 nm
DCB	16.8	1.25	8.62	7.81	9.22	1.5	1.25	115	0.6
OCN	14.7	2.35	6.90	6.62	8.11	1.0	1.0	7	55

As for dechlorination, Zimmerli¹⁴ has shown that PCB mixtures are converted quantitatively into biphenyl on a partly deactivated palladium catalyst. Under the same conditions, PCNs are converted into naphthalene and some tetralin. As Zimmerli did not give quantitative data on the behaviour of PCNs, no meaningful conclusions can yet be drawn concerning the merit of so-called carbon-skeleton chromatography.

Hutzinger *et al.*¹² stressed that treatment of PCNs with the powerful perchlorination reagents antimony(V) chloride-iodine and antimony(V) chloride alone leads to extensive degradation of the chlorinated naphthalenes. In our laboratory, it has been demonstrated that complete decomposition also results upon treatment of PCN

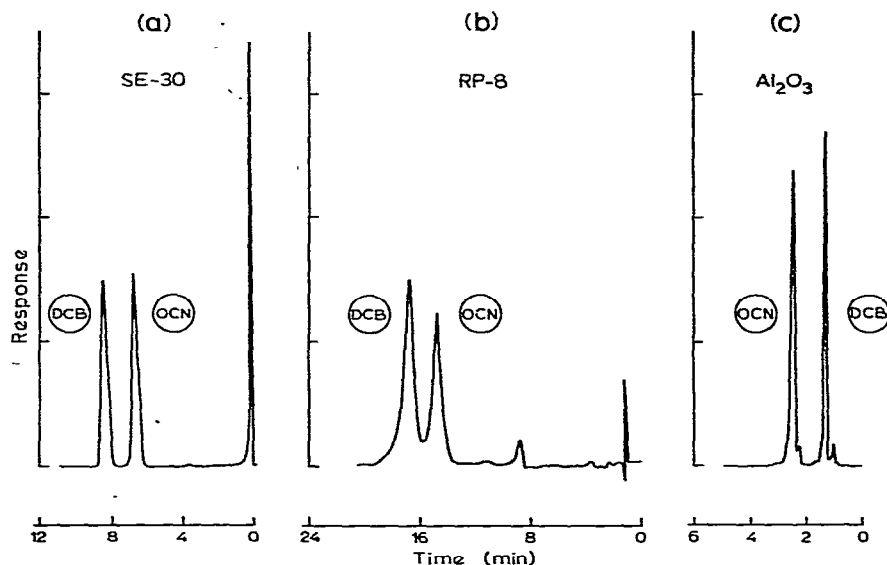


Fig. 1. Separation of DCB and OCN by (a) GC with 1% SE-30 on Chromosorb W as stationary phase at 220°; (b) reversed-phase HPLC on RP-8 using methanol-water (85:15, v/v) as mobile phase (1.2 ml·min⁻¹; temperature, 24°); (c) adsorption HPLC on aluminium oxide with dry *n*-hexane as eluent (2.6 ml·min⁻¹; temperature, 22°).

mixtures such as Halowax 1000, 1099, 1014 and even 1051 with antimony(V) chloride following the procedure of Berg *et al.*¹⁵, as modified by Armour¹⁶. Hence perchlorination of PCN-PCB mixtures appears to be a promising alternative to the chromium trioxide oxidation technique discussed above. The obvious advantage of the perchlorination procedure is the extremely high (electron-capture) detector response of DCB. On the other hand, the chromium trioxide oxidation method leaves the PCBs unaffected, and the peak pattern, and thus the nature of the PCB mixture, remains identifiable.

Recently, several papers from this laboratory¹⁷⁻¹⁹ have been devoted to the analysis of PCN and PCB mixtures by high-performance liquid chromatography (HPLC) in the system silica gel-dry *n*-hexane. The chromatograms of the commercially available mixtures display 10-20 peaks. However, the PCNs are eluted in the same retention time range as the more highly chlorinated PCBs. Despite this unfavourable situation, quantitative discrimination between PCNs and PCBs is possible by means of multiple-wavelength detection¹⁹. In the 275-320-nm region, the PCNs display a series of absorption maxima ($\log \epsilon = 3.7-4.1$), whereas absorption of the PCBs is negligible. On the other hand, PCBs show a strong absorption band between 195 and 215 nm ($\log \epsilon = 4.6-5.1$); here, the absorption due to PCNs is rather small. However, one should realise that detection of PCNs in the 275-320-nm region instead of at their wavelength of maximum absorption, which generally lies between 224 and 244 nm, causes an approximately 10-fold decrease in sensitivity.

As a promising alternative, we can consider the potential of HPLC coupled with perchlorination. In the system silica gel-dry *n*-hexane, the retention times of DCB and OCN are identical^{17,19}, values of 1.65-1.70 min being observed at a flow-rate

of $1.4 \text{ ml} \cdot \text{min}^{-1}$ and a temperature of 27° . However, the spectral characteristics of DCB and OCN are very different, as is evident from the data in Table I. Consequently, detection at 215 and 275 nm opens up the possibility of discriminating between PCNs and PCBs after their perchlorination, as is demonstrated in Fig. 2.

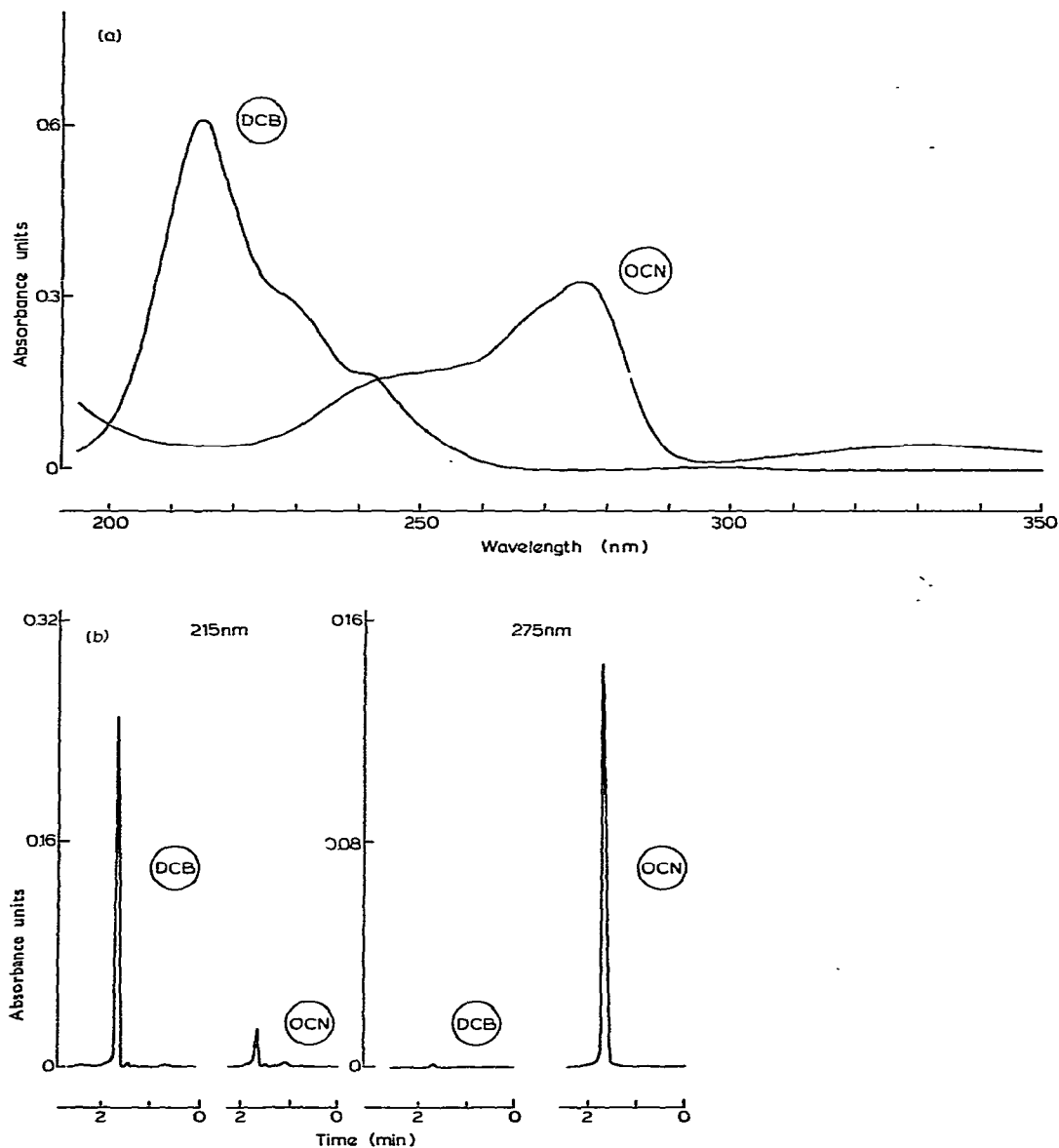


Fig. 2. (a) UV absorption spectra of solutions of *ca.* 20 ppm of DCB and OCN in *n*-hexane (cell path length, 2 mm); (b) HPLC chromatograms of solutions of *ca.* 30 ppm of DCB and OCN in *n*-hexane in the system silica gel (LiChrosorb SI 60)-dry *n*-hexane, using UV detection at 215 and 275 nm. Flow-rate, $1.4 \text{ ml} \cdot \text{min}^{-1}$; temperature, 27° .

Recent research has shown that an adequate separation of DCB and OCN is obtained in HPLC on C_8 reversed-phase material, using methanol containing *ca.* 15% (v/v) of water as the mobile phase (Fig. 1b). From the data in Table II, it can be seen that the capacity ratio of DCB is more strongly dependent than that of OCN on the water content of the mobile phase. As a consequence, at very low water contents, the order of elution changes and DCB precedes OCN. Even better results are obtained in adsorption chromatography on an aluminium oxide column, using dry *n*-hexane as eluent. At a flow-rate of about $2.6 \text{ ml} \cdot \text{min}^{-1}$, the two well resolved peaks show up within 3 min (Fig. 1c). An added advantage of the latter system is that in principle it can easily be coupled with an electron-capture detector, which is impossible with the reversed-phase system.

TABLE II

DEPENDENCE OF k VALUES OF DCB AND OCN ON COMPOSITION OF MOBILE PHASE
System: LiChrosorb RP-8 with methanol-water mixtures; flow-rate, $1.2 \text{ ml} \cdot \text{min}^{-1}$; temperature, 24° .

Methanol-water (v/v)	k	
	DCB	OCN
99:1	1.00	1.10
95:5	1.70	1.85
90:10	3.40	3.40
85:15	14.2	12.4
80:20	39.5	25.3

Further applications

The various chromatographic systems recommended here for the separation of OCN and DCB should also offer good opportunities for the separation of other highly halogenated aromatic compounds. An example is the analysis of Halowax 1051. In a previous paper²⁰, it was reported that OCN and both heptachloronaphthalenes can effectively be separated from each other on a C_8 reversed-phase column, using methanol-water (9-8:1-2, v/v) as the mobile phase. However, the time of analysis is rather long (*ca.* 20 min). Improved results have now been obtained in both GC and HPLC, as is evident from Fig. 3. Admittedly, the GC separation of the hepta-substituted naphthalenes with OV-17 as the stationary phase, although rapid, is poor [to our surprise, we observed that OV-17 does not separate DCB and OCN; on the other hand, SE-30, which effectively separates the latter two compounds (see above), does not separate the heptachloronaphthalenes]. The HPLC separation on the aluminium oxide column is rapid and gives a good resolution.

CONCLUSION

In practice, the selection of a particular technique will be determined by two main factors: (1) the importance of recognizing the chromatographic pattern of the PCBs and PCNs; (2) the concentration level of the polychlorinated compounds in the sample solution. If pattern recognition is not of primary importance, one will often select a technique involving a perchlorination step, because this considerably increases the sensitivity of the method and reduces separation problems.

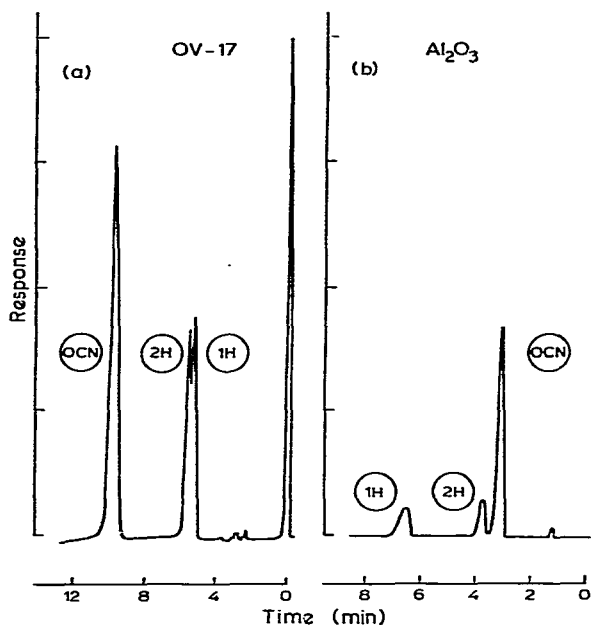


Fig. 3. Separation of OCN and 1H- and 2H-heptachloronaphthalene (a) by GC with 4% OV-17 on Chromosorb W as stationary phase at 275°C (column, 2.50 m × 1 mm I.D.) and (b) by HPLC on aluminium oxide with dry *n*-hexane as eluent; flow-rate, 1.4 ml·min⁻¹; temperature, 27°C.

In this paper, three methods of analysis are reported that permit an efficient separation of DCB and OCN. With samples that contain very low levels of PCNs and PCBs, no doubt analysis by electron-capture GC will be favoured. At present, analysis by electron-capture HPLC still gives detection limits that are higher by about an order of magnitude, as can be gathered from data on organochlorine pesticides published by Willmott and Dolphin²¹. If higher levels of chlorinated biphenyls and naphthalenes are present in the sample solution, we recommend the use of HPLC instead of GC, because it is more convenient and, with the aluminium oxide system, a more rapid technique. In our opinion, future developments should be directed primarily at the enhancement of sensitivity in the HPLC procedures, e.g., by evaluating more thoroughly the merits of the electron-capture detector coupled to liquid chromatographic systems. Alternatively, the use of relatively large injection volumes, which easily decreases the limiting concentrations of sample solutions by an order of magnitude, can be recommended^{22,23}.

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