

CHROM. 10,945

## ANALYSIS OF POLYCHLORINATED NAPHTHALENES, POLYCHLORINATED BIPHENYLS AND POLYCHLORINATED TERPHENYLS VIA CARBON SKELETON GAS-LIQUID CHROMATOGRAPHY

MICHAEL COOKE, GRAHAM NICKLESS, AILEEN M. PRESCOTT and DAVID J. ROBERTS

*Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 ITS (Great Britain)*

(Received February 15th, 1978)

---

### SUMMARY

Mixtures of polychlorinated naphthalenes (PCNs), polychlorinated biphenyls (PCBs) and organo-chlorine pesticides have been determined by carbon skeleton gas chromatography (GC). Polychlorinated terphenyls (PCTs) have also been investigated. Using hydrogen as the carrier gas, on-column catalytic reduction of PCNs to naphthalene was quantitative for a 3% palladium catalyst at 305°. PCBs were reduced to biphenyl and PCTs to a mixture of *o*-, *m*-, and *p*-terphenyl under similar conditions. PCBs and PCNs were also analysed successfully on a 5% platinum catalyst at 180°. The products of catalytic reduction were identified by GC-mass spectrometry. The method allows detection of nanogram quantities of polychlorinated species.

---

### INTRODUCTION

The analysis of environmental samples containing residues of organochlorine pesticides in association with polychlorinated naphthalenes (PCNs) and biphenyls (PCBs) is a difficult process due to the essentially similar nature of these three groups of compounds. Pre-chromatographic clean-up procedures *via* thin-layer chromatography or column chromatography<sup>1-4</sup> have been used to separate the three classes with success, but organo-chlorine pesticides (OCPs) such as aldrin, heptachlor and *p,p'*-DDE tend to remain in the PCB fraction. Separation of PCBs from PCNs has not been reported. Further simplification of the matrix has been achieved<sup>5</sup> by using a chromium trioxide catalyst to oxidise *p,p'*-DDE but this procedure causes complete loss of PCNs prior to determination. High-performance liquid chromatography has been used with some success<sup>6</sup> to characterise PCNs, separation from the low-chlorinated PCBs being achieved. However, more highly chlorinated PCB mixtures, common OCPs and polychlorinated terphenyls (PCTs) are eluted in the retention time region characteristic of PCNs. Qualitative, and more especially quantitative analysis of the PCB and PCN contribution to environmental contamination has thus proved extremely difficult.

Carbon skeleton gas chromatography (GC), first reported by Thomson *et al.*<sup>7</sup>

and later developed by Beroza<sup>8</sup> and Beroza and Sarmiento<sup>9</sup> allows direct analysis of many organic compounds such as acids, anhydrides, alcohols and aldehydes by catalytic conversion to the parent hydrocarbon followed by GC. This procedure involving the direct coupling of a catalytic converter to the gas chromatograph was later applied by Asai *et al.*<sup>10</sup> and Zimmerli<sup>11</sup> to the analysis of OCPs and PCBs. However, under the conditions employed mixtures of products were obtained. More recently, nickel boride (NiB<sub>2</sub>) with excess NaBH<sub>4</sub> has proved effective in the dechlorination of DDT, heptachlor and chlordane<sup>12</sup>.

Recent work has suggested that OCPs, PCBs and PCNs may be present together in Severn Estuary sediments<sup>13</sup>, but identification is uncertain. We now report the development of a catalytic method for the analysis of environmental samples containing OCPs, PCBs and PCNs in which the PCB and PCN components are converted to biphenyl and naphthalene, respectively. OCPs of the DDT family (DDT, DDE and TDE) are converted to the parent C<sub>14</sub> hydrocarbon.

## EXPERIMENTAL

### Reagents

All chromatographic columns were prepared by standard procedures. All standard solutions were prepared in distilled hexane unless solubility required the use of diethyl ether. Naphthalene, biphenyl and terphenyl isomers were purified by recrystallisation (three times) prior to use. Concentrations of PCN and PCB standards were equivalent to 1000 ppm solutions of naphthalene or biphenyl (Table I). Because of impurity problems (see Results and Discussion) commercial PCTs were made up as 1000 ppm solutions.

TABLE I

WEIGHTS OF PCBs OR PCNs EQUIVALENT TO 1  $\mu$ g OF BIPHENYL OR NAPHTHALENE FROM DEFINITION OF COMPOUND OR MICROANALYSIS

PCB mixture	% Cl (def. of compound)	Equivalent ( $\mu$ g)	PCN mixture	% Cl (microanalysis)	Equivalent ( $\mu$ g)
1232	32	1.45	D88	51.4	1.99
1242	42	1.69	D116N	54.9	2.14
1248	48	1.87	D130	56.8	2.25
1254	54	2.11			
1260	60	2.38			

**3% Palladium catalyst.** The required amount of palladium chloride (Johnson Matthey, Royston, Great Britain) was dissolved in 50 ml of hot 5% acetic acid and the support (Chromosorb P, Jones Chromatography, Glamorgan, Great Britain) added. Sodium hydroxide was added to neutralise both the anion of the metallic salt solution and the acetic acid. Evaporation of solvent and drying (110°, 12 h) produces the catalyst.

**5% Platinum catalyst.** The support was added to a 5% solution of platinum chloride, evaporated to dryness and dried (100°, 12 h).

After careful packing onto the chromatography column, catalysts were con-

ditioned, under a stream of hydrogen at 120° (30 min), then 240° (30 min), and finally at 310° for 6 h. The previously reported conditions for activating catalysts appear to be much too short.

### Equipment

A normal Pye 104 gas chromatograph fitted with dual flame ionisation detectors (FID) was used. The carrier gas (hydrogen) was adjusted to 40 ml/min, and the air supply to the flame was 280 ml/min. No hydrogen was supplied directly to the FID since the carrier gas flow was sufficient. The column was extended to provide the catalyst chamber which was heated with an electric furnace controlled by a Variac variable transformer (Fig. 1). The detector oven was set at 300°.

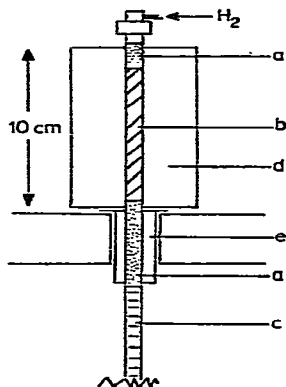


Fig. 1. Catalyst oven arrangement. a, Glass wool; b, catalyst; c, column packing; d, catalyst oven; e, injection port heater.

GC-mass spectrometry (GC-MS) studies were carried out using a V.G. Micromass MM16B mass spectrometer coupled to a Pye 104 gas chromatograph via a single-stage jet separator. For GC-MS studies the following conditions were employed: ionising potential, 50 eV; accelerating voltage, 4 kV; interface temperature, 250°; source temperature, 200°; carrier gas, 30 ml/min.

### RESULTS AND DISCUSSION

Previous work<sup>10,11</sup>, using a 1% palladium catalyst activated to 300° and then partially deactivated by injection of sulphur in CS<sub>2</sub>, yielded a mixture of bicyclohexyl, phenylcyclohexyl and biphenyl from PCBs. We have found that the partial deactivation, either with sulphur in CS<sub>2</sub> or with sulphur in hexane, is an uncontrollable, and therefore unreliable, process. However, a 3% palladium catalyst, fully activated, will reduce PCNs to naphthalene and PCBs to biphenyl. DDT, DDE and TDE are converted to 1,1'-diphenylethane (C<sub>14</sub>H<sub>14</sub>) and PCTs are converted to terphenyl (C<sub>18</sub>H<sub>14</sub>). PCNs are readily reduced but conditions for the dechlorination of PCBs exclusively to biphenyl are critical. At low catalyst temperatures (< 275°) hydrogenation of the aromatic rings may occur as an alternative reaction. Temperature variation of the catalyst from 140° up to 305° showed progressive decrease in the formation

of bicyclohexyl ( $C_{12}H_{22}$ ) and phenylcyclohexyl ( $C_{12}H_{16}$ ) together with a corresponding increase in the yield of biphenyl ( $C_{12}H_{10}$ ). At  $305^\circ$  biphenyl was the exclusive product from the Arochlors used. It seems likely that, at low temperatures, loss of chlorine is followed by, or coupled with, hydrogenation of the aromatic rings. At higher temperatures a secondary reaction, involving the dehydrogenation of the cyclic system is also present.

Dechlorination of PCNs was much easier. At low catalyst temperatures ( $< 280^\circ$ ) hydrogenation of the aromatic rings was less pronounced although GC-MS studies indicated that some tetrahydronaphthalene ( $m/e = 132$ ) was present. At temperatures above  $280^\circ$  naphthalene was the exclusive product from the PCN mixtures used. At  $305^\circ$  PCN were quantitatively converted to naphthalene.

Polychlorinated terphenyl mixtures such as 5432 and 5460 were converted to a mixture of *o*-, *m*- and *p*-terphenyl. 5432 also revealed a small biphenyl content suggesting that chlorinated biphenyls may be present in this mixture. The biphenyl content of 5460 is much larger being *ca.* 5% of the total. The mixture 6040, upon catalysis, yielded four major components. Approximately half the total column effluent was identified as biphenyl, ( $m/e = 154$ ), the remainder consisting of the three terphenyl isomers. GC-MS studies suggested the presence of traces of other components in these mixtures. Of particular note were two minor constituents with  $m/e = 168$  and  $m/e = 228$ .

With 5% (w/w) platinum as the catalyst, and employing temperatures from  $205^\circ$  to  $305^\circ$  conversion of PCNs was unsatisfactory. At  $205^\circ$  naphthalene alone yielded two compounds, tentatively identified as tetra- and decahydronaphthalene, but at higher temperatures peak height for equivalent concentration decreased indicating decomposition. PCNs yielded the same two compounds as naphthalene but conversion efficiency decreased with increasing temperature. At  $305^\circ$  no peaks were observed, presumably due to complete destruction of the naphthalene skeleton.

Complete destruction of PCBs was also accomplished on passage through the catalyst at  $305^\circ$ . At  $280^\circ$  small amounts of bicyclohexyl ( $m/e = 166$ ), phenylcyclohexane ( $m/e = 160$ ) and biphenyl were eluted. Progressive reduction of the catalyst temperature resulted in an increase in both the relative and absolute amounts of bicyclohexyl. At  $180^\circ$  the sole product was bicyclohexyl and conversion was quantitative. Under similar conditions PCNs were converted to a single component identified as decahydronaphthalene ( $m/e = 136$ ). These observations support the hypothesis that aromatic structures are produced by a secondary reaction involving the catalytic dehydrogenation of the polycyclic aliphatic species produced by dechlorination of PCNs, PCBs and PCTs.

Partial deactivation of the platinum catalyst by sulphur was only temporarily successful, full activity being spontaneously regained after 1-2 h use.

Conversion efficiencies for the compounds and catalysts used are given in Table II. Efficiency was estimated by comparison of peak height between a PCN or PCB sample after catalysis and the peak height obtained from an equivalent amount of naphthalene or biphenyl (Table I) after passage through the catalyst. Comparison of peak heights for aliquots of naphthalene and biphenyl chromatographed on two similar columns, one with and one without a catalyst pre-column, demonstrated that loss of either component on passage through a catalyst was not significant. Calibration curves obtained from D88 (naphthalene) and 1248 (biphenyl) were linear for the two

ranges 25–150 ng and 150–750 ng, suggesting that overloading of the catalyst was unlikely. Conversion of 1-chloronaphthalene and the three PCN mixtures was quantitative but conversion of three of the PCB mixtures was not (Table II). However, conversion of biphenyl compounds containing from one to four chlorine atoms was quantitative which suggests that a high degree of chlorine substitution leads to a lower conversion efficiency. Sterically protected chlorine atoms such as those *ortho* to the bridge in biphenyl appeared to be removed as easily as sterically exposed ones.

TABLE II  
CONVERSION EFFICIENCIES (%) FOR PCNs AND PCBs

Compound	3% Pd (305°)	5% Pt (180°)	Compound	3% Pd (305°)	5% Pt (180°)
C <sub>10</sub> H <sub>8</sub>	100	100	C <sub>12</sub> H <sub>10</sub>	100	100
C <sub>10</sub> H <sub>7</sub> Cl	100	99	C <sub>12</sub> H <sub>9</sub> Cl	100	100
D88	101	99	1232	100	98
D116N	96	97	1242	100	98
D132	102	96	1248	84	97
			1254	86	96
			1260	83	96

Detection levels for PCBs and PCNs were good. Using an FID, injections corresponding to 10 ng of Arochlor 1248 or the PCN D88 gave biphenyl or naphthalene peaks with a signal to noise ratio of greater than 30:1. Using a GC-MS system in the single ion mode ( $m/e = 128$  for naphthalene,  $m/e = 154$  for biphenyl) 1-ng injections of PCB or PCN yielded a full-scale deflection on the recorder (20 mV sensitivity).

Typical examples of carbon skeleton gas chromatograms are shown in Figs. 2 and 3. Fig. 2a represents a mixture of Arochlor 1248 and D88 before catalysis and Fig. 2b the carbon skeleton chromatogram. Peaks 1 and 2 were identified by GC-MS and by comparison with standards as naphthalene and biphenyl, respectively. Likewise Fig. 3a represents a mixture of Arochlor 1248, the PCN D88 and the organochlorine pesticides dieldrin, aldrin, heptachlor, *p,p'*-DDT, *p,p'*-DDE and *p,p'*-TDE. These six were selected because of their common use in Great Britain. Fig. 3b is the

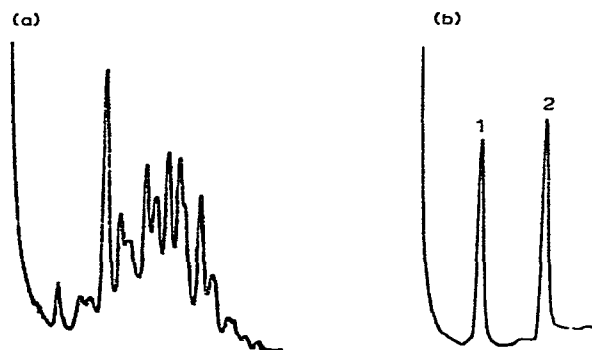


Fig. 2. (a) Arochlor 1248 (1000 ppm) and D88 (100 ppm) before catalysis and (b) after catalysis. Injections were 1  $\mu$ l. Column, 5% SE-30 on Chromosorb P.

carbon skeleton chromatogram of this mixture. Again peaks 1 and 2 were identified as naphthalene and biphenyl. Peak 3 ( $m/e = 182$ ;  $m/e = 167$ ) appears to be 1,1'-diphenylethane (M.W. = 182), the peak at  $m/e = 167$  corresponding to loss of a methyl group to yield a diphenylmethylcarbonium ion. DDT, DDE and TDE would all yield 1,1'-diphenylethane upon dechlorination. Clearly none of the OCPs present interferes with either the naphthalene or the biphenyl peaks.

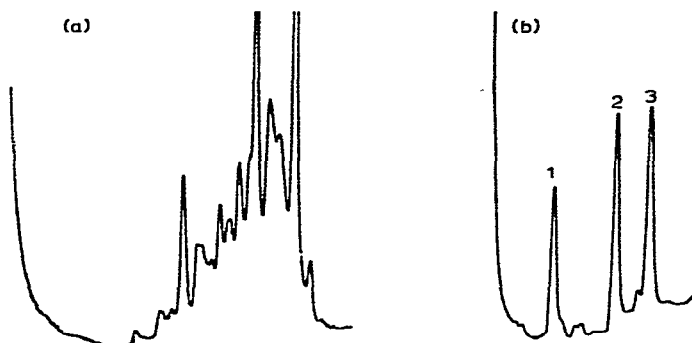


Fig. 3. (a) Arochlor 1248 (1000 ppm), D88 (1000 ppm) aldrin (475 ppm), dieldrin (500 ppm), heptachlor (525 ppm), *p,p'*-DDT (425 ppm), *p,p'*-DDE (475 ppm), and *p,p'*-TDE (450 ppm) before catalysis and (b) after catalysis. Injections were 1  $\mu$ l. Column, 5% SE-30 on Chromosorb P.

## CONCLUSIONS

As the three groups of compounds considered do not interfere with one another, sample preparation may be reduced to a simple extraction procedure such as cyclic steam distillation<sup>14</sup>. The detection level is much improved since the constituent compounds of a PCN or a PCB mixture are "added" together to form a single component. An on-column concentration step is thus achieved. Although absolute values for the concentrations of the polychlorinated mixtures are not obtained, concentrations in terms of equivalents of naphthalene or biphenyl are more relevant since weathering and biological activity causes changes in the components of the mixture thus changing its original character. Discrimination between, and quantitation of, PCNs and PCBs may thus be achieved. Results of our studies of the levels of PCN, PCB and DDT contamination of environmental samples will appear elsewhere. Preliminary results show that no serious interferences occur from other compounds present in the environment.

The method is particularly suitable to the examination of PCT mixtures. Normally this group of compounds are difficult to study by GC methods because of their low volatility. Polybrominated species may also be catalysed to the parent hydrocarbon but differentiation between chloro- and bromo-species is thus rendered impossible.

## REFERENCES

- 1 L. Fishbein, *J. Chromatogr.*, 68 (1972) 345.
- 2 J. Sherma, *Advan. Chromatogr.*, 12 (1975) 141.

- 3 L. M. Reynolds, *Bull. Environ. Contam. Toxicol.*, 4 (1969) 192.
- 4 N. V. Fehringer and J. E. Westfall, *J. Chromatogr.*, 57 (1971) 397.
- 5 D. C. Holmes and M. Wallen, *J. Chromatogr.*, 71 (1972) 652.
- 6 U. A. Th. Brinkman, A. de Kok, H. G. M. Reymer and G. de Vries, *J. Chromatogr.*, 129 (1976) 193.
- 7 C. J. Thompson, H. J. Coleman, R. L. Hopkins, C. C. Ward and H. T. Rall, *Anal. Chem.*, 32 (1960) 1762.
- 8 M. Beroza, *Anal. Chem.*, 34 (1962) 1801.
- 9 M. Beroza and R. Sarmiento, *Anal. Chem.*, 35 (1963) 1353.
- 10 R. I. Asai, F. A. Gunther, W. E. Westlake and Iwata Yukata, *J. Agr. Food Chem.*, 19 (1971) 398.
- 11 R. Zimmerli, *J. Chromatogr.*, 88 (1974) 65.
- 12 W. H. Dennis and W. J. Cooper, *Bull. Environ. Contam. Toxicol.*, 17 (1977) 57.
- 13 P. Stephens, *B.Sc. Thesis*, University of Bristol, Bristol, 1975.
- 14 G. D. Veith and L. M. Kiwus, *Bull. Environ. Contam. Toxicol.*, 17 (1977) 631.