CHROM. 15,236

DETERMINATION OF POLYCHLORINATED NAPHTHALENES IN THE PRESENCE OF POLYCHLORINATED BIPHENYLS BY CAPILLARY GAS CHROMATOGRAPHY

PHILLIP A. KENNEDY, DAVID J. ROBERTS and MICHAEL COOKE*

School of Chemistry, University of Bristol, Bristol BS8 1TS (Great Britain)

(Received July 26th, 1982)

SUMMARY

Use of a heterogeneous hydrodechlorination reaction requiring the *in situ* generation of $(Ni_2B)_2 \cdot H_3$ by treatment of $NiCl_2$ with $NaBH_4$ in isopropanol allows the quantitation of polychlorinated naphthalenes (PCNs) in the presence of polychlorinated biphenyls. An analytical method is outlined in which sediment samples are first steam-extracted to remove organochlorine compounds from the matrix. The naphthalene content of the extract is then measured. The extract is then hydrodechlorinated and the naphthalene content determined again. The difference in concentration of the naphthalene is then related to the PCN content of the sediment.

INTRODUCTION

The determination of organochlorine pesticide residues (OCPs) in extracts of environmental samples is a difficult and complex procedure[1]. The presence of multi-component industrial compounds such as polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) in the extracts[2,3] interferes with the determination of OCPs[4]. PCBs and PCNs have similar chemical properties and, as both are multi-component compounds, the determination of one group of compounds in the presence of the other group is extremely difficult (see below). Possibly for this reason reports of PCB contamination of the environment are many, yet few reports of contamination by PCNs have appeared. However, PCNs were as commonly used in industry as PCBs.

A mixture of PCBs and PCNs may be physically separated from OCPs by chromatography on silica gel (deactivated with 3 % water)–Celite (4:1)[5] and also on a silica gel–alumina column[6,7] but this separation is extremely difficult to control. However, in these procedures PCBs and PCNs are carried through in the same fraction. Thus, if either PCBs *or* PCNs are to be determined, then the other group of compounds will constitute a source of interference as their respective gas–liquid chromatographic (GLC) elution regions overlap considerably. There is thus a need for a method capable of determining PCNs in the presence of PCBs and *vice versa*. One such technique developed with this aim in mind requires perchlorination of the poly-

chlorinated species to either octachloronaphthalene or decachlorobiphenyl. These two compounds are then quantitated by GLC using an electron-capture detector and the respective concentrations related back to the original compounds. Perchlorination requires treatment of the PCNs and PCBs with antimony pentachloride in a sealed glass vial at 160°C for 15 h, deactivation of excess $SbCl_5$ with 6 M hydrochloric acid and extraction with hexane. This procedure has many disadvantages not the least of which are: the reagents are dangerous, the reaction time is long and the results are unreliable being high by as much as a factor of 2 in the case of PCBs. However the principle of simplification of a complex mixture by chemical reaction prior to analysis is a valid one.

The alternative reaction which provides a chemical simplification of complex organochlorine mixtures is hydrodechlorination. Compounds of industrial significance such as PCBs and PCNs as well as agrochemicals such as toxaphene are made by chlorination of a single parent hydrocarbon. For these three examples the parent hydrocarbons are biphenyl, naphthalene and camphene. Hence controlled hydrodechlorination of the mixture of polychlorinated and isomeric compounds will yield a single hydrocarbon product which may be easily chromatographed as its retention characteristics will, in general, be less than those of the chlorinated species. Identification and quantitation of the parent hydrocarbons is a relatively simple procedure and the concentration may be related back to the original mixture of polychlorinated species[8].

Hydrodechlorination may be achieved by several different methods. For a gas phase reaction we have used either palladium or platinum coated on an inert support as a catalyst. This is placed in the injection port of a gas chromatograph and thus heated. With hydrogen as both carrier and reagent gas, injection of a mixture of organochlorine compounds onto the catalyst results in a rapid hydrodechlorination reaction[9]. The resultant hydrocarbons may be separated by gas chromatography and then identified by mass spectrometry[10,11] and quantitated. The determination of trace amounts of organochlorine pesticides such as p,p'-DDT by this route provides results in excellent agreement with those obtained by more conventional methods[8]. This technique can also be modified for use with capillary columns[12].

Alternatively hydrodechlorination may be carried out in the liquid phase. In contrast to the gas phase technique where reaction times are extremely short, reaction times in the liquid phase range from a few minutes to a few hours. Several different reagents may be used. Relatively complex reaction conditions similar to those required for the perchlorination reaction are necessary when aluminium hydride and alkoxy aluminium reagents are employed[13,14]. Reaction times of several hours have been reported.

An alternative procedure[15] requiring the generation of an active, finely divided nickel boride catalyst as a suspension in isopropanol provides a much simpler reaction system. Reaction times vary according to the compounds being studied but are relatively short. Thus PCBs are completely dechlorinated in 60 min and PCNs in only 10 min (see below). The reaction proceeds at ambient temperature in air and uses no toxic or hazardous reagents. We have previously used a rapid, on-column hydrodechlorination reaction to determine PCBs and PCNs together, However the ease, speed and simplicity of the reaction involving $(Ni_2B)_2 \cdot H_3$ renders it particularly suitable for incorporation into an analytical method for the determination of poly-

chlorinated aromatic species. Its suitability is reinforced by the relative lack of reactivity towards chlorinated cyclodienes (e.g. chlordan[16]), and towards chlorinated alkanes[17].

We now report a method for the determination of PCNs in the presence of PCBs in which a hydrodechlorination step using $(Ni_2B)_2 \cdot H_3$ is applied as a sample preparation procedure prior to determination by capillary gas chromatography.

EXPERIMENTAL

All solvents were distilled before use. Standard solutions were prepared in dry, distilled hexane. The 2 M nickel chloride solution was prepared in distilled water. The 5 M sodium borohydride solution was freshly prepared before each reaction from 1.89 g $NaBH_4$, 0.1 g (approx.) NaOH and distilled water (10 ml). Naphthalene, biphenyl, 2,3-dimethylnaphthalene, nickel chloride, sodium borohydride (all from BDH, Poole, Great Britain), Nibren wax D88 (Bayer, Leverkusen, G.F.R.), and Aroclor 1248 (Monsanto, Newport, Great Britain) were used as received.

A 2451 series capillary gas chromatograph (Erba Science, Swindon, Great Britain) fitted with a Grob type split/splitless injector system, flame ionization detector (FID), and fused-silica column (SP 2100, 12 m × 0.2 mm, Hewlett-Packard) was used. Other parameters were: carrier gas (hydrogen) flow-rate (1.5 ml min^{-1}); injection port temperature 250°C; detector temperature 250°C; temperature programme 60°C hold 1 min, increase 6°C min^{-1} to 200°C, increase 10°C min^{-1} to 210°C, hold 210°C 3 min, cool. Attenuation was × 16 unless otherwise stated. Chart speed was 5 mm min^{-1} for all chromatograms. Injection volume was normally 1 μl.

Quantitation was achieved by use of peak height ratios against an internal standard (2,3-dimethylnaphthalene). Several standard mixtures were prepared with varying amounts of naphthalene and biphenyl and a constant amount of internal standard. Plots were then made of the peak height ratios of, for example, naphthalene–internal standard against concentration of naphthalene. For naphthalene the calibration line equation was $y = 0.054x - 0.430$ ($r = 0.991$) and for biphenyl $y = 0.057x - 0.263$ ($r = 0.996$) where y = peak height ratio, x = concentration of component and r = correlation coefficient.

The optimum conditions for the dechlorination of PCBs have been reported previously[15]. These same conditions were used when PCNs were present. Isopropanol was used as the solvent (see below). The efficiency of hydrodechlorination was measured by replicate (11) reactions on a standard pool containing the Nibren wax D88 (183.2 ppm) and Aroclor 1248 (232.4 ppm). The naphthalene and biphenyl formed were determined for each reaction.

The naphthalene and biphenyl equivalents of D88 and 1248 used were 199 ppm D88 ≡ 100 ppm naphthalene and 187 ppm Aroclor 1248 ≡ 100 ppm biphenyl.

Steam extraction efficiency was assessed from a spiked sample (50 g) of silica gel (60–80 mesh, for chromatography) containing $2.26 \cdot 10^{-4}$ g g^{-1} D88 and $2.86 \cdot 10^{-4}$ g g^{-1} Aroclor 1248. Approximately 2 g of this silica gel were weighed accurately into a 500-ml round-bottomed flask and distilled water (250 ml) and heptane (7 ml) were added and the sample was steam extracted for 3 h (for steam extraction apparatus see ref. 18 but 1/3 scale). The heptane layer was quantitatively removed, reduced to 2 ml under a stream of nitrogen and hydrodechlorinated in isopropanol. The internal standard was introduced after hydrodechlorination.

Sediment samples were collected in glass vessels and stored at 0°C prior to extraction. Weighed amounts of wet samples (*ca.* 200 g) were blended with approx. 1 l distilled water and steam extracted (3 h) from a 2-l round-bottomed flask. Approximately 1 g of NaOH pellets was added to each sample to prevent foaming and the sample was extracted into *ca.* 7 ml heptane. The steam extract was quantitatively transferred, reduced to 2 ml and hydrodechlorinated in isopropanol. A second aliquot from each sediment sample was spiked with a PCN and a PCB [2 ml of a mixed solution of D88 (183 ppm) and Aroclor 1248 (234 ppm) to give an approximate "sediment concentration" of 2 ppm] and treated as above. After extraction sediment samples were dried and weighed.

RESULTS AND DISCUSSION

Hydrodechlorination of PCBs by "nickel boride" has been reported previously[15]. We have used this reaction to hydrodechlorinate polychlorinated naphthalene compounds. With undecane as the internal standard the production of the naphthalene and biphenyl during the course of the reaction was plotted against time to give Fig. 1. Clearly the hydrodechlorination of PCNs proceeds extremely fast under these conditions with complete reaction being achieved in about 10 min. In contrast full hydrodechlorination of the PCB (Aroclor 1248) used took about 60 min. On addition of the sodium borohydride to the reaction mixture a finely divided black precipitate was produced. The reaction was thus a heterogeneous rather than a homogeneous one and probably required a liquid–solid interaction to occur. Presumably therefore the ease of interaction between the polychlorinated aromatic species and the surface of the nickel boride catalyst influences the rate of reaction. Hence the planar
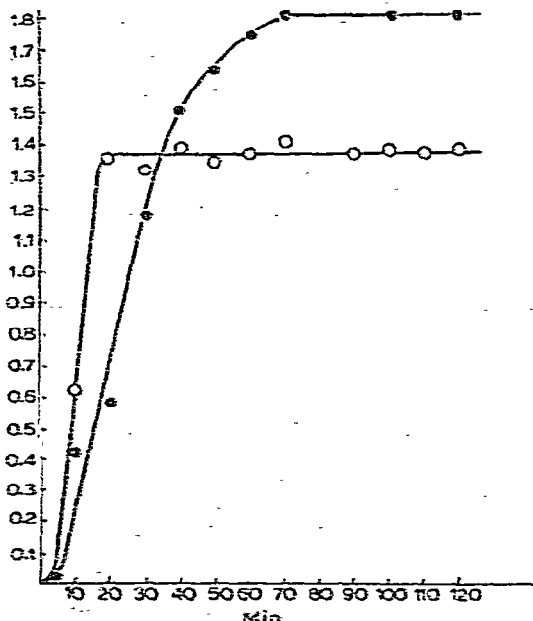

Fig. 1. The hydrodechlorination of PCNs and PCBs using $(Ni_2B)_2 \cdot H_3$ in isopropanol. O, Naphthalene/undecane ratio; ●, biphenyl/undecane ratio.

naphthalene compounds will react more readily than the non-planar biphenyl com-
pounds which may have to coordinate via one ring and then the other sequentially in
order to achieve full hydrodechlorination. For the analysis of PCNs therefore a
reaction time of 10 min is sufficient. The course of the reaction was followed by GLC
using a packed column (2 m × 0.4 cm; 3 % Carbowax 20M on Gas-Chrom Q). The
dramatic simplification of the reaction mixture is shown in Fig. 2. The solvent used
affects the course of the reaction. With isopropanol the sole product from the PCN is
naphthalene. If the solvent is ethanol then the major product is naphthalene but a
significant amount of tetralin (ca. 15–20 %) and a trace of decalin is produced. If the
solvent is methanol then the major product is decalin (a full report of this solvent
effect will appear elsewhere). Identification was by mass spectrometry and correlation
with library spectra. From these experiments isopropanol was selected as the solvent
for the hydrodechlorination reaction. The optimum reaction times selected were 10
min for PCNs and 75 min for PCBs.

The results of 11 replicate hydrochlorination reactions are shown in Table I.
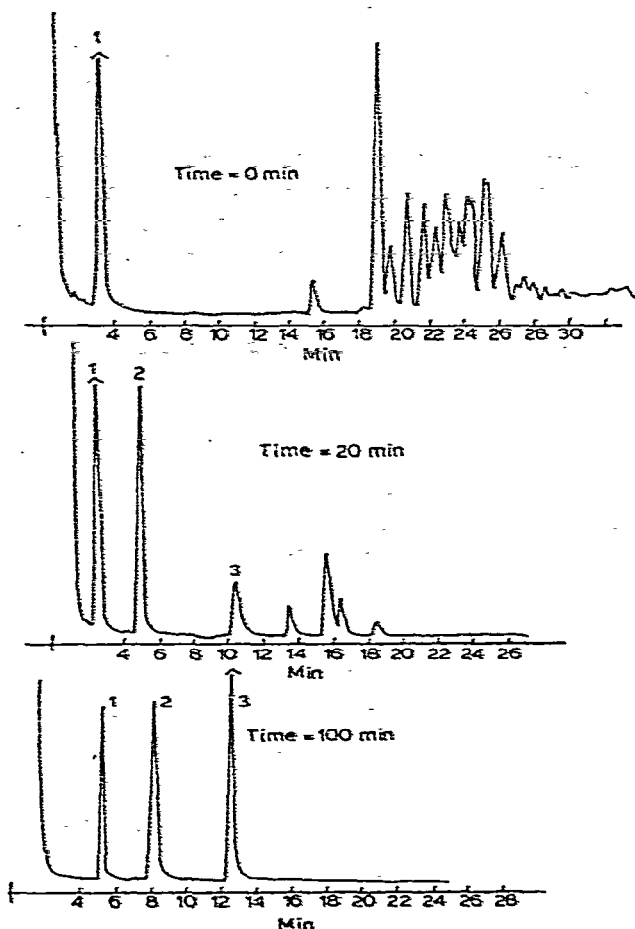

Fig. 2. Chromatograms showing the changing profile of a PCN and PCB mixture during hydrodechlori-
nation in isopropanol.

TABLE I

EFFICIENCY OF HYDRODECHLORINATION OF PCNs AND PCBs

Reaction No.	Naphthalene yield (% of theoretical maximum)	Biphenyl yield (% of theoretical maximum)
1	86.9	72.9
2	87.7	73.3
3	88.4	23.6
4	86.9	39.2
5	98.7	29.0
6	82.4	47.8
7	80.9	35.4
8	91.4	53.6
9	79.3	66.5
10	81.8	73.4
11	86.9	65.0
Mean	86.4	52.8
Standard deviation	5.45	18.8
Relative standard deviation	6.31%	35.7%

The mean value for naphthalene produced (86.4%) and relative standard deviation (R.S.D.; 6.31%) indicate a near quantitative and reproducible reaction. In contrast, the conversion of biphenyl is relatively inefficient and unreliable (R.S.D., 35.7%). This result is somewhat surprising as the hydrodechlorination of polychlorinated biphenyls has been reported as quantitative[18].

The proposed analytical method for PCNs consists of three stages. These are removal of the organochlorine compounds from the matrix by cyclic steam extrac-

TABLE II

EFFICIENCY OF COMBINED STEAM EXTRACTION AND HYDRODECHLORINATION OF PCNs AND PCBs

Sample No.	Naphthalene yield (% of theoretical maximum)	Biphenyl yield (% of theoretical maximum)
1	52.6	51.5
2	61.2	24.0
3	73.2	54.8
4	68.3	33.9
5	55.5	42.8
6	58.0	66.8
7	57.8	49.7
8	56.5	58.6
9	64.3	67.0
10	62.7	65.1
Mean	61.0	51.4
Standard deviation	6.28	14.4
Relative standard deviation	10.3%	28.0%

TABLE III

DETERMINATION OF PCN AND PCB CONCENTRATION IN RIVER SEDIMENTS

	River 1	River 2	River 3
Wt. of sample (g, dry weight)	209.4	123.2	149.9
Concn. PCN found (ppm)	0.00	0.00	0.00
Concn. PCB found (ppm)	0.00	0.00	0.00
Concn. PCN added (found) (ppm)	1.75 (1.58)	2.97 (2.61)	2.44 (2.11)
Concn. PCB added (found) (ppm)	2.22 (0.43)	3.77 (1.18)	3.10 (1.66)
Recovery* for PCN (%)	90.5	88.1	86.7
Recovery* for PCB (%)	19.4	31.5	53.7

* Allowing for extraction and hydrodechlorination efficiency (Table II).

tion, hydrodechlorination to simplify the extract and determination by capillary GLC. To determine the efficiency of the combined first and second stages, a standard sediment sample was prepared. Clean, acid-washed sand was spiked with PCN and PCB and 10 samples were weighed out, steam extracted (2 h) and hydrodechlorinated. The results are given in Table II. The recovery and conversion efficiency for PCNs showed only a small standard deviation but, again, the results for PCBs were
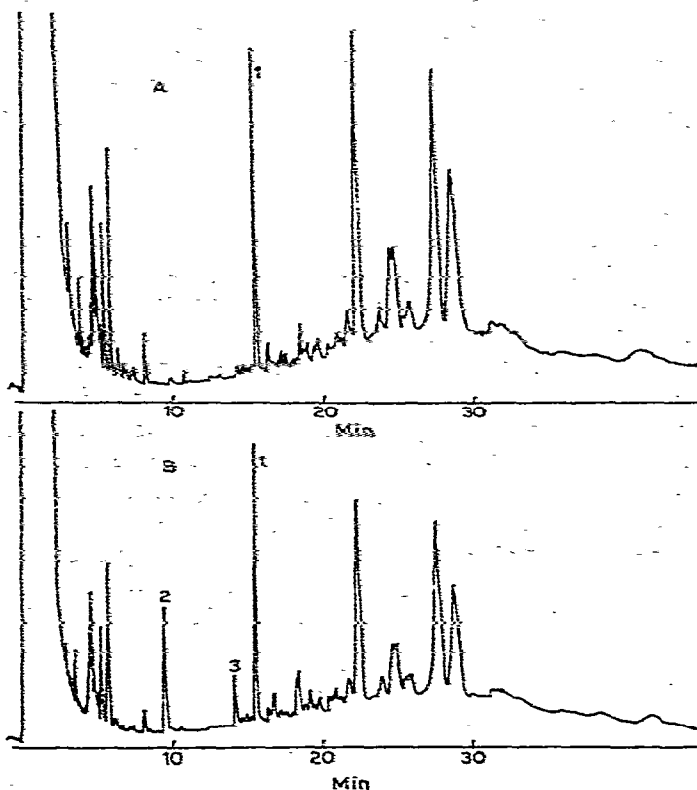

Fig. 3. (A) Extract of river sediment before hydrodechlorination; (B) After hydrodechlorination. 1 = Internal standard, 2 = naphthalene, 3 = biphenyl.

variable. Steam extraction of PCBs from sediments is a reliable and efficient process[10,19] and so these results presumably reflect the variation of the hydrodechlorination step. From these figures the implied recovery of PCN from the sediment was *ca.* 70%.

Quantitation was achieved by comparison of peak heights with an internal standard. Internal standard 2,3-dimethylnaphthalene was selected because it was readily available, eluted close to both naphthalene and biphenyl and does not appear to be present in sediment samples*.

Analysis of river sediments

To test the validity of this method for the determination of PCNs in the presence of potential interferents such as PCBs three samples of river sediments were collected. These were taken from sites thought to be typical of rivers in an urban environment but they were not expected to be contaminated with either PCNs or PCBs. Each sample was taken through the analysis procedure and the concentrations of PCBs and PCNs determined. None were found. A duplicate sample from each site was then spiked with PCN and PCB (added in acetone to the wet sediment and allowed to equilibrate for several hours with loss of acetone by evaporation). Organochlorine compounds were added to give values of 2–3 ppm in the sediment as these values were thought to be typical of contaminated sediments. These spiked samples were then analysed and the PCN and PCB content determined. These results are given in Table III and demonstrate an excellent correlation for the PCN content. Fig. 3 shows capillary gas chromatograms of a sediment sample before (A) and after (B) hydrodechlorination of PCN and PCB.

CONCLUSIONS

The basis of an analytical method which discriminates between PCNs and PCBs has been established. Steam extraction of samples followed by hydrodechlorination and determination by capillary GLC yields accurate values for the PCN content of samples after recovery factors are taken into account. The advantages of this approach are the elimination of potential interference from PCBs, simplicity and brevity. Thus sample simplification via hydrodechlorination results in several important improvements over existing methods. For example a concentration step results in improvements as many chlorinated compounds (poor FID response) are transformed into a single hydrocarbon (good FID response). Chromatographic separation from other compounds is thus more easily achieved. Analysis time is only a few hours, being a combination of steam extraction (2 h) hydrodechlorination (10 min) and capillary gas chromatography (20 min). We are currently using this method to reinvestigate sampling sites on the River Severn and a full account of these results will appear elsewhere.

---

* This internal standard may be unsuitable for use with biota such as shell- and other fish where it has been observed[20].

REFERENCES

1 *Manual of Analytical Methods For The Analysis of Pesticide Residues In Human and Environmental Samples*, EPA 600/8-80-038, U.S. Environmental Protection Agency, Environmental Toxicology Division, Research Triangle Park, NC, 1980.
2 L. Fishbein, *J. Chromatogr.*, 68 (1972) 345.
3 S. Jensen, *New Scientist*, 32 (1966) 612.
4 J. A. Armour and J. A. Burke, *J. Ass. Offic. Anal. Chem.*, 54 (1971) 175.
5 J. A. Armour and J. A. Burke, *J. Ass. Offic. Anal. Chem.*, 53 (1970) 761.
6 A. V. Holden and K. Marsden, *J. Chromatogr.*, 44 (1969) 481.
7 V. Zitko, *Int. J. Environ. Anal. Chem.*, 1 (1972) 221.
8 M. Cooke, K. D. Khallef, G. Nickless and D. J. Roberts, *J. Chromatogr.*, 178 (1979) 183.
9 M. Cooke, G. Nickless, A. M. Prescott and D. J. Roberts, *J. Chromatogr.*, 156 (1978) 293.
10 M. Cooke, G. Nickless, A. C. Povey and D. J. Roberts, *Sci. Total. Environ.*, 13 (1979) 17.
11 M. Cooke, D. J. Roberts and M. E. Tillett, *Sci. Total. Environ.*, 15 (1980) 237.
12 M. Cooke and D. J. Roberts, *J. Chromatogr.*, 193 (1980) 437.
13 H. Panzel and K. Ballschmiter, *Z. Anal. Chem.*, 271 (1974) 182.
14 G. Seidl and K. Ballschmiter, *Z. Anal. Chem.*, 296 (1979) 281.
15 W. H. Dennis and W. J. Cooper, *Technical Report 7702*, U.S. Army Medical Bioengineering Research and Development Lab., Fort Detrick, MD, 1977.
16 G. M. Sawula Musoke, M. Cooke and D. J. Roberts, *Bull. Environ. Contam. Toxicol.*, 28 (1982) 467.
17 M. Cooke, unpublished results.
18 W. H. Dennis, Jr., Yun H. Chang and W. J. Cooper, *Bull. Environ. Contam., Toxicol.*, 22 (1979) 750.
19 G. D. Veith and L. M. Kiwus, *Bull. Environ. Contam. Toxicol.*, 17 (1977) 631.
20 P. Donkin, personal communication.