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Limitations in the Use of Nickel Boride Dechlorination for the Analysis of Polychlorinated Biphenyls

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The determination of polychlorinated biphenyls (PCBs) in environmental samples presents the analyst with many problems. PCBs occur as complex mixtures in the environment at variable concentrations ranging from the low ppb to the ppm level. Most sample extracts need to be subjected to an extensive cleanup procedure prior to GC analysis. An electron-capture detector is the most commonly used detector but cleanup procedures may still let electron-capturing species remain in the extract, so the identities of the eluting peaks must be confirmed.

In order to overcome some of these problems, perchlorination of the PCBs has been used; this gives rise to one GC peak (decachlorobiphenyl) which is well removed from most interfering peaks, but this technique has been found to be qualitatively and quantitatively unreliable (De Kok et al. 1982; Duinker et al. 1980). Dechlorination has also been proposed (Dennis et al. 1979; De Kok et al. 1980; Kennedy et al. 1982) but we find that this also is unsatisfactory and do not recommend its use.

MATERIALS AND METHODS

A nickel boride dechlorination method (Dennis & Cooper 1977; Dennis et al. 1979) was employed whereby a precipitate of nickel boride is produced **in situ** according to the reaction:

$$9H_2O + 2NiCl_2 + 4NaBH_4 \longrightarrow 12.5H_2 + 4NaCl + 3H_3BO_3 + Ni_2B$$

(Dennis & Cooper 1975)

A total of fifteen experiments were performed; they fell into three groups:

i) Solutions of each of three Aroclors (1242, 1248 and 1260, 5 mL of approximately 150 µg/mL each) were placed in 250-mL round bottomed (r.b.) flasks. 2-Propanol (25 mL) and 2M $NiCl_2$ (aq. 0.5 mL) were added.

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To each of these was added, dropwise, 30 mmol of $NaBH_4$ dissolved in 4 mL of distilled water. Thus, each reaction mixture comprised approximately:

$$\begin{array}{c} \text{PCB} : \text{Ni}^{2+} : \text{NaBH}_4 \\ 2.8\ \mu\text{mol}:1000\ \mu\text{mol}:30000\ \mu\text{mol} \end{array}$$

in 25 mL of 2-propanol + 4.5 mL of water + 5 mL of n-heptane.

The mixture was allowed to react, with stirring, for 2 h at room temperature after which time 100 mL of distilled water was added. The reaction products were then extracted with n-heptane and made up to a known final volume.

ii) Solutions of each of the three Aroclors in n-heptane (5 mL of 15 μg/mL) were placed in 250-mL r.b. flasks and evaporated just to dryness over air. $NaBH_4$ powder (500 mg) was added to each. 2-Propanol (0.5 mL) and distilled water (0.5 mL) were added; then 2M $NiCl_2$ (aq. 0.3 mL) was added dropwise. So, each reaction mixture comprised approximately:

$$\begin{array}{c} \text{PCB} : \text{Ni}^{2+} : \text{NaBH}_4 \\ 0.3\ \mu\text{mol}:\ 600\ \mu\text{mol}:13000\ \mu\text{mol} \end{array}$$

in 5 mL of 2-propanol + 0.8 mL of water.

The mixture was allowed to react, with stirring, at room temperature for 75 min. Distilled water (150 mL) was then added to the flasks followed by concentrated HCl dropwise until no further hydrogen was produced. The mixture was then steam extracted for 3 h by using a Nielson-Kryger unit (Veith & Kiwus 1977) into n-heptane and diluted to a known final volume.

iii) A solution of PCB (4 mL of 131 μg/mL Aroclor 1260 + 125 μg/mL Aroclor 1242) in n-heptane was pipetted into a 25-mL r.b. flask. This was evaporated just to dryness in a rotary evaporator at 45°C. $NaBH_4$ powder (1.0 g) was added followed by 8 mL of 2-propanol. 2M $NiCl_2$ (aq. 1 mL) was then added, dropwise, so the reaction mixture comprised approximately:

$$\begin{array}{c} \text{PCB} : \text{Ni}^{2+} : \text{NaBH}_4 \\ 3.3\ \mu\text{mol}:2000\ \mu\text{mol}:27000\ \mu\text{mol} \end{array}$$

in 8 mL 2-propanol + 1 mL of water.

The reaction was allowed to proceed for 45 min at room temperature. After this time the reaction mixture was transferred quantitatively to a 100-mL separating funnel with about 70 mL of distilled water and extracted with n-heptane. The extract was made up to a known final volume.

All organic solvents were of high purity and analyses were performed by using capillary GC with a 25 m 0.35 mm i.d. SE-30 equivalent column. Flame ionisation detection was employed. Quantitative work was performed using either 4-chloro-m-cresol or 4,4'-dibromobiphenyl as internal standard.

RESULTS AND DISCUSSION

Experiments in group (i) gave seven main peaks plus a very small amount of reduced biphenyl (probably phenylcyclohexane) for all three Aroclors studied (see Fig. 1). The proportions of the peaks varied slightly depending on the Aroclor used but biphenyl was the main product in every case. The six peaks eluting after biphenyl are mono- and dichlorobiphenyls - probably ortho isomers since, due to steric effects, ortho chlorines are more difficult to remove from the biphenyl nucleus than meta and para chlorines. The presence of the chlorinated biphenyls also confirms the observation of Kozloski (1985) that n-alkanes reduce the efficiency of the nickel boride catalyst. There was no significant residue of higher chlorinated biphenyls left in the sample. Recoveries were not determined.

Group (ii) experiments gave biphenyl in good yield but left a small amount of monochlorobiphenyl remaining and also produced significant amounts of reduced biphenyl (see Fig. 2). The recovery results are shown in Table 1.

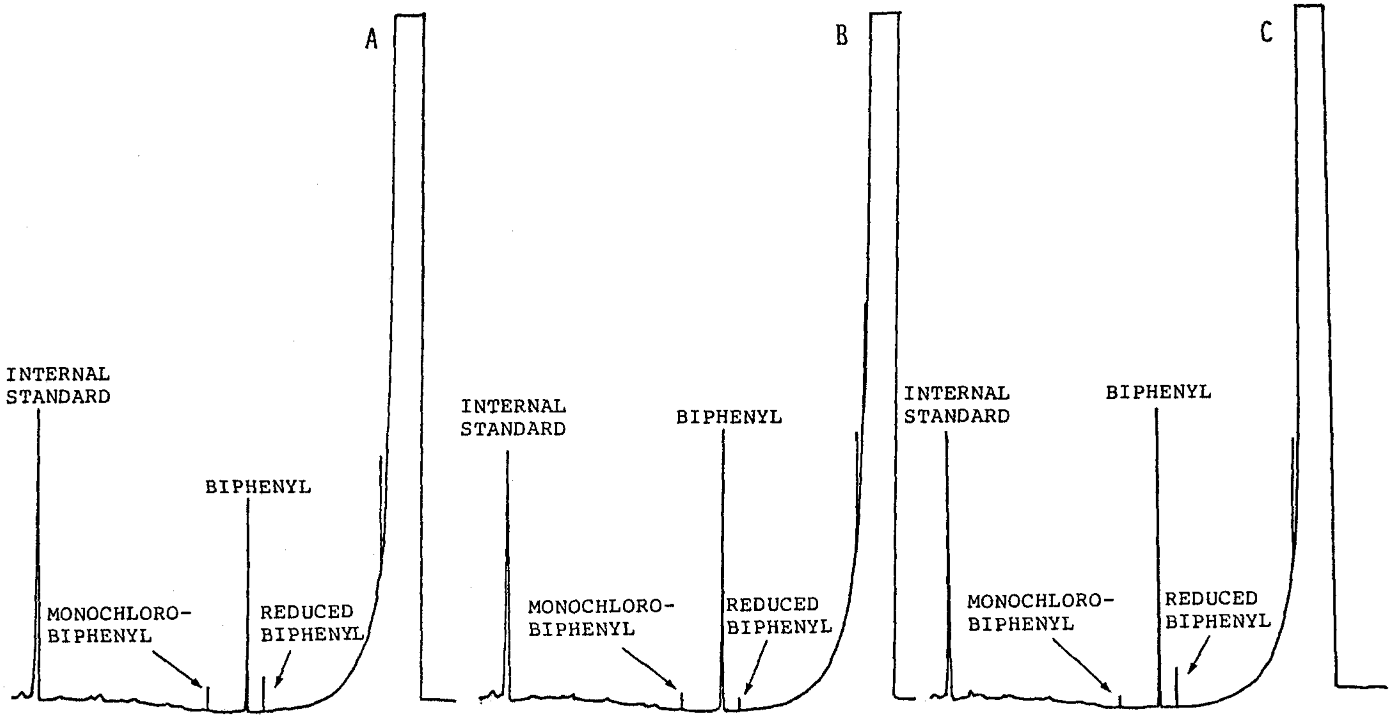
Table 1. Recoveries from group(ii) dechlorination experiments.

PCB Source	Mean recovery of biphenyl expressed as percentage of theoretical yield.	Mean total recovery expressed as percentage theoretical yield of biphenyl.*
Aroclor 1242	74 %	83 %
Aroclor 1248	75 %	80 %
Aroclor 1260	58 %	73 %

* Based on total peak areas.

We have previously validated the efficiency of the steam extraction method for biphenyls and PCBs (**unpublished results**) and found it to be almost 100% efficient at the levels being considered when extracting from aqueous media.

The production of reduced biphenyl in significant amounts demonstrates that the activity of the catalyst is not immediately destroyed by the addition of the concentrated HCl. The nickel boride dissolves under the action of the acid after boiling for about three min in the steam extraction apparatus, to give a pale green solution (presumably of $NiCl_2$). In the time between heating the reaction mixture and the dissolution of the catalyst, the conditions in the flask seem to be suitable for reducing the biphenyl nucleus. Under these conditions, it may be expected that any chlorines remaining on the biphenyl ring system would be removed. That this is not so may be due to the chloride ions from the acid in some way attacking the aromatic system, assisted by the catalytic surface.



(A) AROCLOR 1260 (B) AROCLOR 1248 (C) AROCLOR 1242

Figure 1 Group (i) Dechlorination Experiments

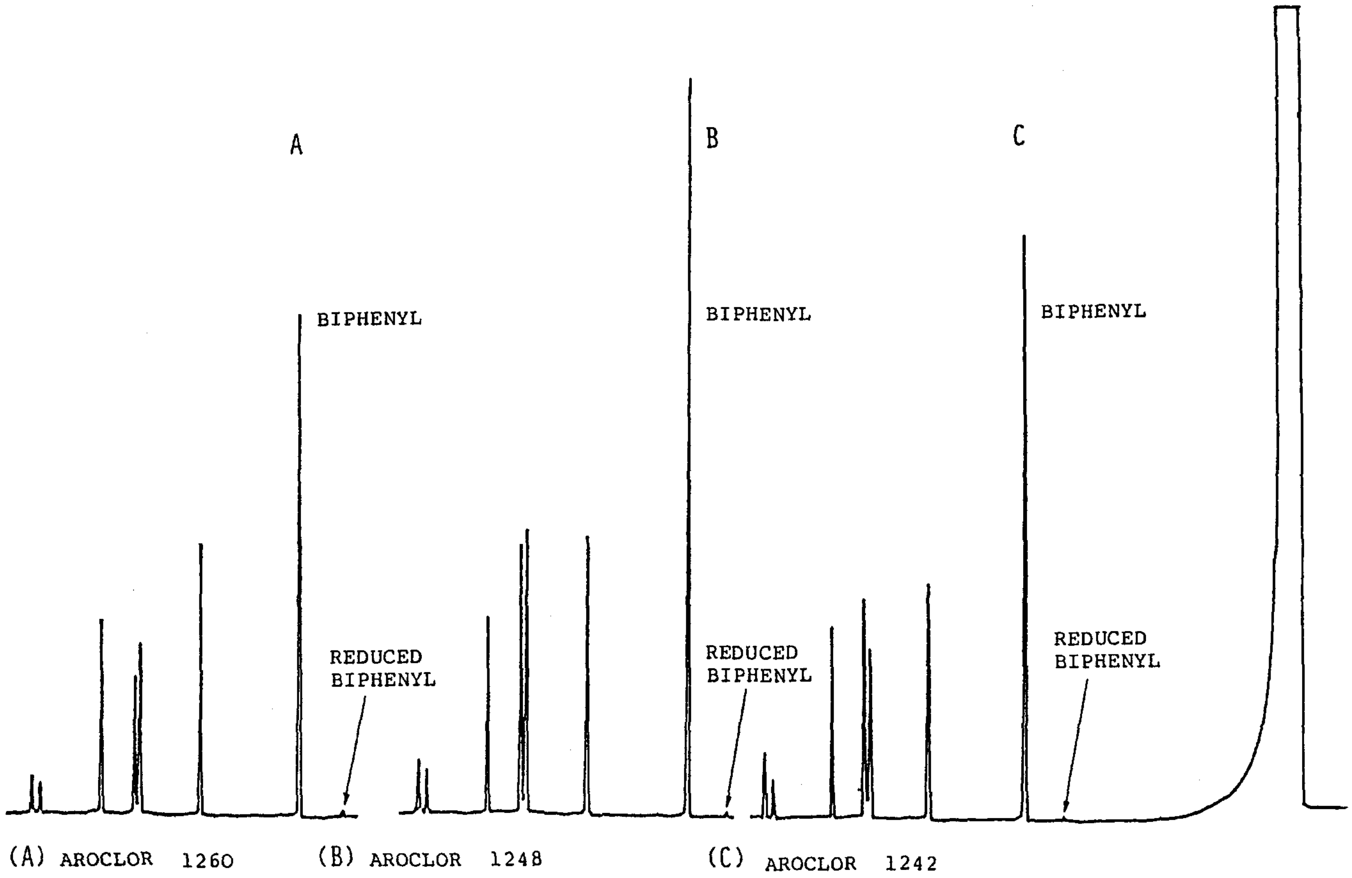


Figure 2 Group (ii) Dechlorination Experiments

Experiments in group (iii) illustrate the fact that it is possible to obtain biphenyl as the sole product although a small amount of a monochlorobiphenyl (about 3% of total peak area) did remain in one sample (see Fig. 3). Recoveries for replicates varied from 75% to 82% of theoretical yield of biphenyl.
It can be seen that this dechlorination method has many shortcomings. The procedure is sensitive to reaction conditions and extraction methods. It is noteworthy that De Kok et al. (1982) found dechlorination with $LiAlH_4$ also gave variable and possibly inaccurate results. The best recovery obtained in this laboratory was 85% of theoretical biphenyl yield. The loss may be due to a number of factors including incomplete dechlorination, incomplete extraction and loss of biphenyl by volatilisation.

Biphenyl is a volatile compound and we have found that any attempt to evaporate biphenyl solutions to dryness, particularly over air or in a rotary evaporator, can result in almost total loss of the biphenyl, particularly at low levels.

Another drawback of dechlorination methods is the increase in the limit of detection. Biphenyl is not significantly electron-capturing so GC-ECD cannot be used. Consequently, a flame ionisation detector must be employed or, if using an HPLC method, a UV detector. These detectors may not be sufficiently sensitive to detect the low levels of biphenyl produced by dechlorination of environmental samples. GC-MS does give a much lower limit of detection but may not be routinely available to the analyst.

Biphenyl itself is also an environmental contaminant and unless it is removed (e.g. by oxidation) from samples prior to the dechlorination step, it could artificially inflate the result obtained for PCBs.

Overall, the method is not satisfactory for the routine analysis of PCBs in environmental samples. The procedure is not sufficiently robust or reliable and the reaction requires the use of expensive reagents in considerable quantities.

The current trend in PCB analysis is towards the use of accurate congener-specific capillary GC methods (Ballschmiter & Zell 1980; Bush et al. 1983; Safe et al. 1985). This allows the analyst to produce congener-by-congener assay results for toxicological evaluation. It is known that different PCB congeners display different toxicological profiles (Poland & Glover 1977; Safe 1984) and so analyses which provide the toxicologist with congener-specific data on the chlorinated biphenyls are far more meaningful than a method, such as perchlorination or dechlorination, which merely gives a single (possibly inaccurate) result for total PCB concentration. Congener-specific methods are also less involved in that the chemical modification of the PCBs is avoided thus eliminating one step in the assay procedure.

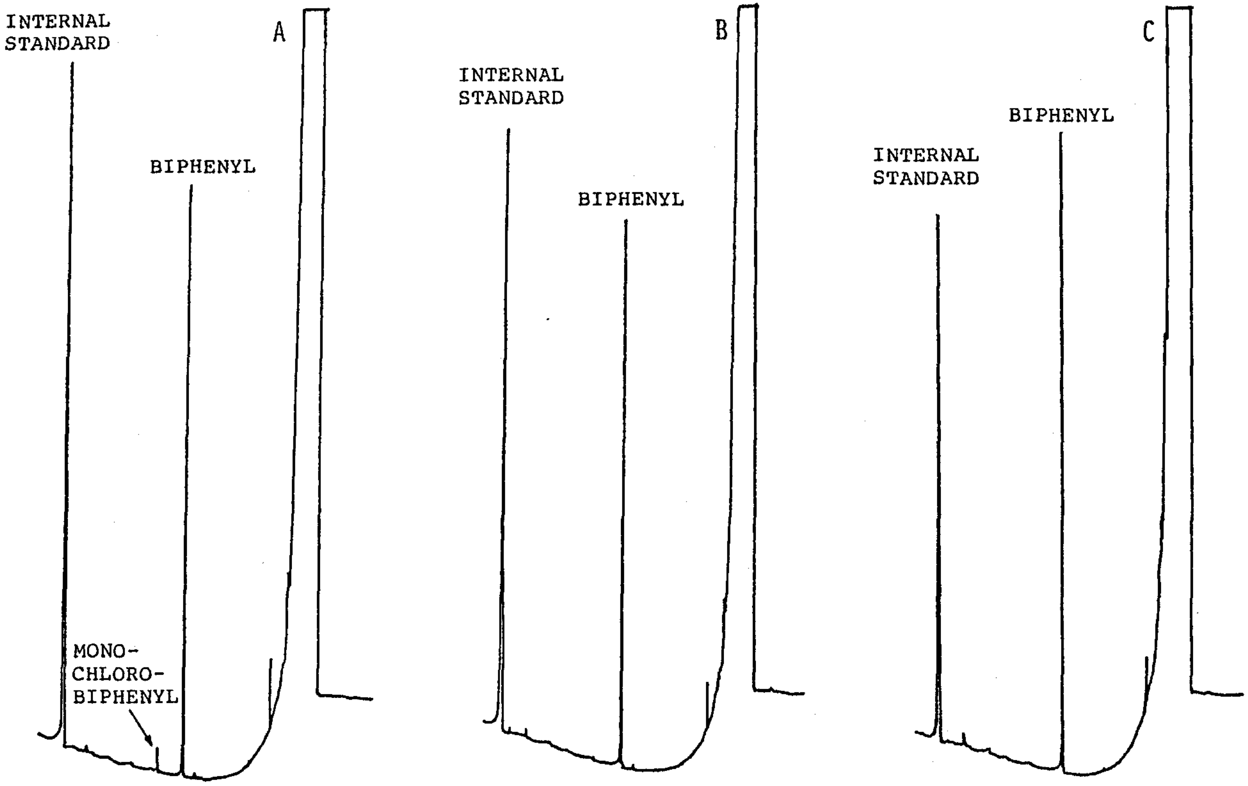


Figure 3 Replicate Group (iii) Dechlorination Experiments

We believe that dechlorination methods of PCB analysis should, on the whole, be rejected for the reasons outlined above, in favour of congener-specific analyses which, in the absence of major interferences, seem to provide more accurate and meaningful data.

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