# Retention Times and Electron-Capture Detector Responses of Some Individual Chlorobiphenyls

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Retention times and electron-capture detector responses of 23 chlorobiphenyls are reported in this paper. Polychlorinated biphenyls (PCB) are global pollutants (1) and gas chromatography has been used to determine PCB in the environment (2,3,4). Only commercial PCB preparations, containing mixtures of chlorinated biphenyls are commonly available as standards and more knowledge of the behaviour of the individual chlorinated biphenyls during gas chromatography is desirable. Retention times and electron-capture detector responses have been reported for mono- and dichlorobiphenyls (5,6). An excellent separation method for mono-, and some di- and trichlorobiphenyls by gas chromatography on polyphenyl thioethers has been patented (7). As a general rule, chlorine substitution in position 2 shortens and vicinal disubstitution lengthens the retention time. The reported relative electron-capture detector responses are 1, 0.2, 2.3, 7.6, 5.8, and 3.5 for 4-, 3-, 2-mono-, 4,4'-, 3,3'-, and 2,2'-dichlorobiphenyl, respectively (6).

## Experimental

The preparation and characterization of the individual chlorinated biphenyls is described elsewhere (8). A Packard A7901 gas chromatograph with a glass column (6 ft x 4 mm), containing 4% SE-30 on acid-washed Chromosorb W, 100/120 mesh, operated at 200°C, was used. Carrier gas was nitrogen at a flow rate of 60 ml/min. Injector and detector were kept at 210°C. D.C. voltage in the electron-capture detector was 95V and meter sensitivity was $1 \times 10^{-8}$ Amp. Solutions of chlorinated biphenyls in pesticide-grade hexane were used, a 25:75 v/v mixture of pesticide-grade benzene and hexane was required to dissolve decachlorobiphenyl. Concentration of chlorinated biphenyls in solutions injected on the column was 1 - 260 µg/ml, and volumes from 2 to 5 µl were injected to obtain peak heights of 30-70% of the full scale pen deflection. Areas under the peaks were measured by a disc integrator. Every compound was injected at least four times to check the linearity of the detector response. p,p'-DDE was used as the standard. Total peak area was used as the



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MONS 084949

detector response for the two commercial polychlorinated biphenyl preparations, Aroclor 1254 and Aroclor 1260.

## Results and Discussion

Relative retention times and electron-capture detector responses of chlorinated biphenyls and of Aroclor 1254 and 1260 are presented in Table 1. Both the retention time and the detector response depend on the number of chlorine atoms in the molecule and on the substitution patterns. Chlorine substitution in positions 2 and 6 shortens, and vicinal substitution lengthens, the retention time also in tri- and tetrachlorobiphenyls. In some instances these effects overshadow the effect of the number of chlorines in the molecule which increases the retention time.

The detector response increases strongly with increasing number of chlorine atoms in the molecule. Thus the response of decachlorobiphenyl is 500 times stronger than the response of 4-chlorobiphenyl. Most of the increase occurs in the mono- to trichlorobiphenyl range and the response increases only by a factor of approximately 2-3 between tetra- (with the exception of 2,2',4,4'- and 2,2',6,6'-tetrachlorobiphenyl) and decachlorobiphenyl. Chlorine substitution in positions 2 and 6 decreases and vicinal substitution, particularly in positions 3 and 4, increases the electron-capture detector response.

Polychlorinated biphenyls found in wildlife are of the Aroclor 1254 or 1260 type (2,3,4). These Aroclors give under our conditions 14 and 16 peaks with relative retention times from 0.48 to 3.28 and from 0.72 to 6.80, respectively. Additional chlorinated biphenyls will have to be prepared to be able to identify the components of Aroclor 1254 and 1260. The presented data do indicate, however, that the electron-capture detector response of all chlorinated biphenyls with 4-9 atoms of chlorine per molecule is not likely to exceed the value of 1.6 relative to p,p'-DDE under the described conditions.

MONS 084950

TABLE 1

Retention time and electron-capture detector response of chlorobiphenyls

| Compound | Relative retention time (p,p'-DDE=1.00) | Relative response per ng ± standard deviation (p,p'-DDE=1.00) |
|---|---|---|
| 4-chlorobiphenyl | 0.17 | 0.0033±0.00005 |
| 2- " | 0.11 | 0.0030±0.00004 |
| 3- " | 0.14 | 0.0006±0.00001 |
| 4,4'-dichlorobiphenyl | 0.30 | 0.0152±0.0002 |
| 3,3'- " | 0.25 | 0.0155±0.0001 |
| 2,2'- " | 0.15 | 0.0131±0.0001 |
| 3,4- " | 0.28 | 0.0388±0.0002 |
| 2,4- " | 0.19 | 0.0450±0.0004 |
| 2,6- " | 0.16 | 0.0815±0.0049 |
| 2,4,4'-trichlorobiphenyl | 0.39 | 0.298±0.010 |
| 2,4,6- " | 0.24 | 0.276±0.006 |
| 2,2',4,4'-tetrachlorobiphenyl | 0.51 | 0.206±0.003 |
| 3,3',4,4'- " | 0.96 | 0.770±0.027 |
| 2,2',6,6'- " | 0.33 | 0.0403±0.0016 |
| 3,3',5,5'- " | 0.70 | 0.625±0.045 |
| 2,3,4,5- " | 0.69 | 0.715±0.010 |
| 2,3,5,6- " | 0.51 | 0.505±0.010 |
| 2,3,4,5,6-pentachlorobiphenyl | 1.00 | 1.30±0.017 |
| 2,2',4,4',6,6'-hexachlorobiphenyl | 0.78 | 0.545±0.029 |
| 3,3',4,4',5,5'- " | 2.98 | 1.15±0.064 |
| 2,2',3,3',4,4',6,6'-octachlorobiphenyl | 2.62 | 1.58±0.020 |
| 2,2',3,3',5,5',6,6'-octachlorobiphenyl | 2.45 | 1.53±0.076 |
| Decachlorobiphenyl | 8.20 | 1.61±0.086 |
| Aroclor 1254 | | 0.910±0.008 |
| Aroclor 1260 | | 1.35±0.010 |



MONS 084951

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MONS 084952