

Electron Impact Mass Spectrometric Response Factors and Fragmentation of All 209 PCB Congeners

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Introduction

There are 209 possible polychlorinated biphenyls although the technical polychlorinated biphenyls formulations do not contain all of them. About 140 congeners have been detected in Aroclor 1242, 1254, or 1260 at a concentration above 0.05% (w/w). Some of these are easily degraded in the environment, primarily the less chlorinated ones. The PCB mixtures encountered in nature are however still very complex. Further, PCBs are biomagnifying in biota and are harmful to both wildlife and humans. It is therefore essential to have good tools to separate and accurately quantify these compounds.

Gas chromatography – mass spectrometry (GC–MS) have been widely used for PCB analyses of all kind of environmental matrixes. The technique is both selective and very sensitive. One major problem has been to identify the individual PCBs in the complex mixtures. It has also been difficult to know how to quantify these compounds, as only a few have been widely available as reference compounds. However, in recent years the availability of pure individual PCBs has improved tremendously, and last year all 209 PCBs were available at a reasonable price.

In this study we have used commercial mixtures of PCBs to determine the electron impact mass spectrometric response factors and fragmentation patterns of all 209 PCB congeners

Material and methods

All 209 PCB congeners were obtained from AccuStandard Inc. (New Haven, CT, USA) as nine mixtures in iso-octane. Five of the mixtures contain PCB congeners that are abundant in Aroclor formulations (C-CS-01 through C-CS-05), and four contain PCBs that are absent or less abundant in Aroclors (C-CS-06 through C-CS-09). The concentration of all congeners was 10 µg/mL. An aliquot corresponding to 120 ng was transferred to a GC vial, 310 ng of octachloronaphthalene (OCN) was added as a syringe spike, and the volume was adjusted to 110 µL. Thus, the final concentration of the PCBs and the OCN was 1.1 and 2.8 ng/µL, respectively.

Two microliter aliquots of the PCB mixtures was splitless injected (250 °C) using an autoinjector onto the GC column which was directly interfaced to the ions source (250 °C) of a Fisons MD-800 MS (Manchester, UK). Three different columns were used for this study: (1) 60m × 0.32mm DB-5, 0.25 µm film, 5% phenyl-methylsilicone (J&W, Folsom, CA, USA); (2) 25m × 0.25mm Chirasil-Dex CB, 0.12 µm film, 10% permethylated cyclodextrin linked to a polydimethylsilicone (Chrompack, Middelburg, The Netherlands); (3) 20m × 0.25mm LC-50, 50% liquid chrySTALLINE/ 50% polydimethylsiloxane (J&K Environmental Ltd, Sydney, Nova Scotia, Canada). The analyses were performed in the selected ion recording mode under electron impact (EI) conditions. The two most intense ions of the molecular ion, (M - Cl)⁺, and (M - 2Cl)⁺ clusters were monitored for detection of OCN and mono- through decachlorobiphenyls. The GC oven was temperature programmed as follows: 80 °C (3 min), 3 °C/min to 300 °C, isothermal for 10 min (DB-5); 80 °C (3 min), 3 °C/min to 250 °C, isothermal for 25 min (Chirasil-Dex); 80 °C (3 min), 3 °C/min to 270 °C, isothermal for 20 min (LC-50). Helium was used as carrier gas at a head pressure of 14 psi (DB-5) or 10 psi (Chirasil-Dex and LC-50).

Following analyses all peaks were integrated and the total area of all ions in the isotope distribution clusters were calculated using the theoretical isotope distribution values. The ratio of ion pair monitored for each cluster was used as a quality control parameter to assure that the MS was operating properly. This ratio should be within 5% of the theoretical value.

Results and discussion

Most of the PCB congeners were eluting as single components from the DB-5 column. However, despite the manufacture efforts to design mixtures that do not coelute in GC analyses on 5% phenyl-methylsilicone columns several pairs were unresolved. These had to be separated using one of the other two columns. Chirasil-Dex was used to obtain data for the PCBs 81, 88, 111, 116, 121, 125, 137, 148, 166, and 182, whilst the LC-50 column was used for the PCBs 142, 145, 176, and 188. For three congeners, PCBs 88, 121, 122, and 165, it was impossible to determine the area of the (M - Cl)⁺ ions. These had to be analysed separately.

The molecular ion responses generally decrease with the degree of chlorination, see Table 1 and Figure 1. The highly chlorinated PCBs also exhibit less variability in their responses.

Table 1: EI-MS relative response factors vs. OCN for all PCB homologues.

Species	RRF			
	Max	Min	Average	RSD%
MonoCB	2.758	2.550	2.718	0.080
DiCB	3.268	1.242	2.338	1.085
TriCB	2.335	0.830	1.648	1.532
TetraCB	1.415	0.582	0.970	0.532
PentaCB	1.635	0.620	1.105	0.485
HexaCB	1.348	0.622	0.888	0.390
HeptaCB	0.872	0.415	0.615	0.270
OctaCB	0.872	0.375	0.592	0.352
NonaCB	0.625	0.360	0.528	0.292
DecaCB	0.572	0.572	0.572	

The M⁺ response decrease is partially an imaginary since the data is expressed on weight basis and not on a molar basis. The RRFs are much more similar on a molar basis although the same trend is still observed. The variability differences are probably due to a saturation effect. The chlorines are very electronegative and induce a change in the electronic structure of the biphenyl. The magnitude of the perturbation will depend on the position(s) of the substituents. In the highly chlorinated PCBs the properties of the molecule will not be that substitution dependent as the biphenyl backbone will be depleted of electron density almost independent of the substituent positions. However, there are still a strong structure dependence in relation between molecular and fragment ions, see Figure 1.

To our knowledge this is the first study to report both relative retention time and fragmentation data for all 209 PCBs. Our fragmentation data confirms earlier findings by other groups (e.g. 1-3). Some of the key factors that influence PCB stability are the type of substitution in the four o,o'-positions, the number of adjacent *ortho-meta* chlorines, and the molecular symmetry. However, the space limitations prevent us from including a full discussion of all aspects of the PCB electronimpact MS characteristics in this abstract. That will be covered in our presentation at Dioxin '98 and in future publications.

References

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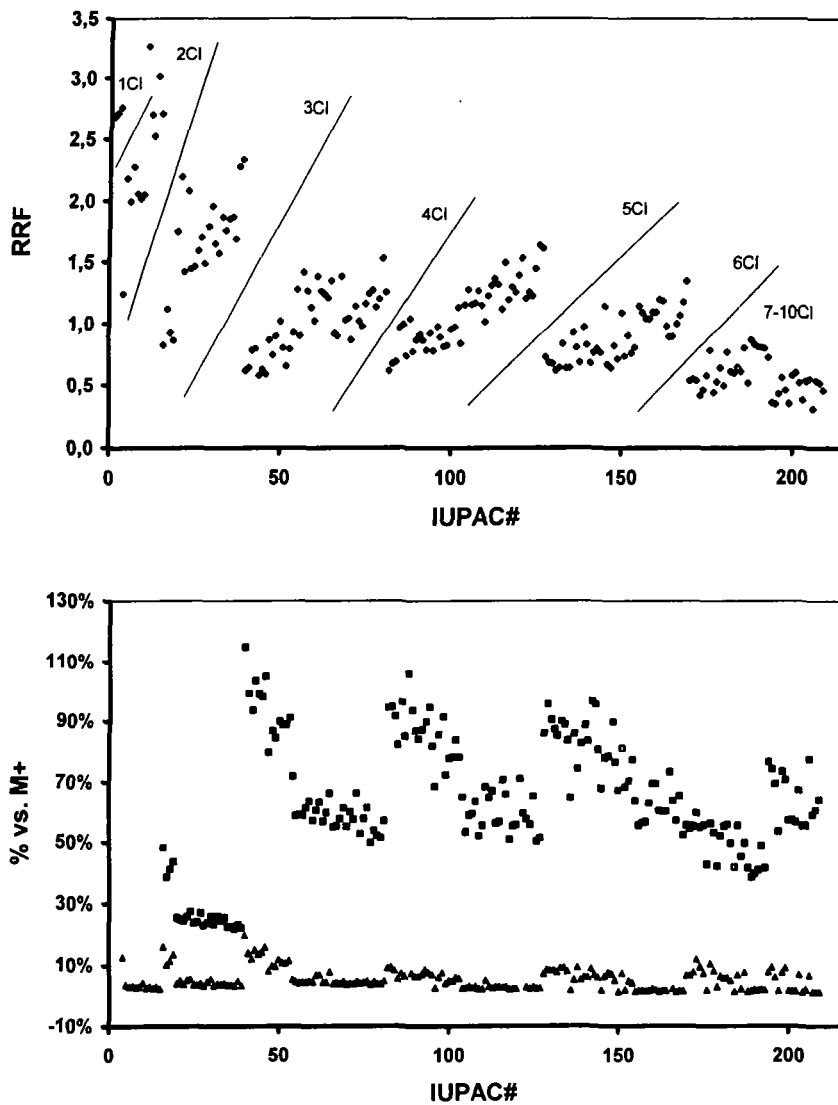


Figure 1: Molecular ion relative response factors of the 209 PCBs (top panel), and $(M-Cl)^+$ (\blacktriangle) and $(M-2Cl)^+$ (\blacksquare) abundances relative to M^+ (lower panel).