A Study of All 209 PCB Isomers using GC-APCI-MS/MS at Various Collision Energies: Correlations with EI Data and Toxicity

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Introduction
This study provides new data on all 209 PCB isomers from GC-MS analyses using a hybrid Q-IMS-TOF mass spectrometer. High-resolution accurate mass data for each isomer was obtained at 5 different collision energies in order to obtain the relative responses of the fragment ions produced.
The aims of this study are to examine correlations between these data and the toxicity of the various congeners, and to compare the spectra formed using atmospheric pressure ionization with those from traditional EI.

Materials and methods
The instrumentation consisted of a Synapt G2-S hybrid Q-IMS-TOF (Waters, Wilmslow, UK) mass spectrometer equipped with a 7890 GC (Agilent, Santa Clara, USA) using SP-1ms and SPB-Octyl (Supelco, Bellefonte, USA) GC columns. Atmospheric pressure chemical ionisation (APCI) using a corona discharge within the source led to positive ion formation.
A series of analyses were performed for mixes of PCB standards with applied collision energies of 0, 10, 20, 30 and 40 volts. Peak responses were then calculated from extracted mass chromatograms from the molecular ion cluster and, where applicable, from fragments due to the loss of both 1 and 2 chlorine atoms. At each chlorination level, 2 traces were created (e.g. M and M+2) to permit isotope ratio verification due to the various ^{35}Cl and ^{37}Cl contributions.

Results and discussion
Results from a pilot study focused on 5 hexa-chlorinated biphenyls (HxCB): PCB-138, 156, 157, 167 and 169 analyzed using collision energies (CE) of 0, 15, 30 and 45 volts. Of these, only PCB-138 is considered non-toxic – a key feature being that it has di-ortho substitutions, i.e. with chlorine atoms in positions 2 and 2', whereas the remainder are either mono-ortho (PCBs 156, 157 & 167) or non-ortho (PCB-169) substituted. The stearic hindrance introduced by having 2 (or more) ortho substitutions is believed to play a role in PCB toxicity in regard to limiting an isomer's ability to bind with the Ah receptor.
With zero volts CE, all 5 HxCBs (injected at nominally equal concentrations) produced similar responses (5% RSD). With the CE increased to 15 V some response changes were noted, but these were all less than 10% relative to 0 V CE.
At 30 V CE significant changes were observed with the responses of PCB-138 at ~4% and the 3 mono-ortho substituted HxCBs at 60~63% relative to PCB-169. Although these mono-ortho PCBs are considered toxic, their assigned toxic equivalent factors are 1/1000th of that assigned to PCB-169. (At 45 V CE all peaks in the M+ traces were practically non-detects.)
The full study confirms these data and expands to examine the relationships for all 209 congeners at various collision energies.