Aroclor (1016 to 1268) and Congener Specific Analysis using New HT8-PCB GC Column

William Mills[1]

[1]Mills Consulting Inc.

Introduction

Polychlorinated biphenyls (PCBs) comprise a class of compounds based on the biphenyl molecule containing one-10 chlorine atoms. In the US, PCBs were primarily produced Monsanto Corporation (St. Louis, MO) from 1929 until the mid-1970's as different mixtures under the trade name "Aroclor". The commercially most important Aroclor's contained ca. 21-68% chlorine by weight, and were designated 1221-1268 .[1] Although there are 209 different PCB molecules possible, Frame[2] has shown that only 144 of these are present in Aroclors 1242, 1254, and 1260 in significant amounts (>0.1% by weight) (Table 1).

Analysis of PCBs in environmental samples is typically performed by Gas Chromatography GC using a wide variety of GC columns. Presently, the DB-XLB has (Agilent Technologies) has been considered to offer the best separation of PCB congeners[3]. A novel gas chromatograph capillary column[4] (SGE 60 m HT8-PCB,) was investigated for its usefulness in performing comprehensive, quantitative, congener-specific (CQCS) PCB analyses[5]. The retention times and coelutions for the 144 major PCB congeners for this new capillary column were determined and compared to the retention times and coelutions for these congeners on two commonly used capillary columns (60 m DB-XLB and 60 m DB-5MS)[5]. Additionally, nine Aroclor mixtures (1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, and the seldom explored 1268) were analyzed and chromatographically compared.

Materials and Methods

Materials/Standards**.** All solvents were Fisher Optima® quality, HPLC-grade or equivalent. PCB mixes 1-5 (AccuStandard, New Haven, CT) designed to allow for analysis of congeners in the individual mixes without coelution interferences were used for the qualitative congener assignments and quantitative calibration of the instruments and are described in detail elsewhere[2]. Aroclor standards (1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268) and individual PCB congeners (*e.g.* PCBs 30, 65, 166, and 204) used for recovery surrogates and internal standards were also purchased from AccuStandard.

Laboratory Methods. Samples were extracted for analysis using soxhlet extraction rotary evaporation, silica gel cleanup and blow down to final volume. PCB 65 and 166 were used for recovery surrogates and PCB 30 and 204 were used for internal standard quantitation. Analysis of NIST SRMs showed results within 10-20% of the reference values.

Instrumental. An Agilent 6890N gas chromatograph (GC) was used for the analysis of all samples. The GC was equipped with a ^{63}Ni electron capture detector, and an Agilent 7683 autosampler. UHP Helium was used as the carrier gas and UHP Nitrogen at 10 mL/min was used for makeup. The 1 µL sample was injected in splitless mode. Inlet temperature =280 °C, Detector 340 °C. GC conditions were as follows: i) 60 m, 0.25 mm HT8-PCB (SGE, Inc, Austin, TX, www.sge.com). Gas flowrate=1 mL/min in constant flow mode. Initial T= 120 °C for 5 min, ramp 20 °C/min to 180 °C, ramp 2 °C/min to 260 °C, ramp 5 °C/min to 300 °C, hold for 5 min. ii) 60 m, 0.25 mm DB-XLB (J&W Scientific, Folsom, CA) carrier gas constant pressure mode= 29 psi , Initial T= 100 °C for 1.3 min, ramp 1.95 °C/min to 293 °C, hold for 10 min. iii) 60 m, 0.25 mm, 0.25 µm DB-5MS (J&W Scientific, Folsom, CA) were based on those for the IADN project[6]. Inlet T=300 °C, Detector= 300 °C, Carrier gas at constant 24 psi, 100°C for 1 min, ramp 1 °C/min to 240 °C, ramp 10 °C/min to 280 °C, and hold for 20 min. UHP argon:methane (95:5) at 10 mL/min was used as the detector makeup gas for these runs. Additional detail on Materials and Methods is provided elsewhere[5]

Results and Discussion

Table 1 provides data on the weight fraction represented by the 144 congeners in Mix 1-5 for 9 Aroclors[7].

TABLE 1: Weight Fraction of Aroclor from 144 Congener (PCB Mix 1-5)[7]

Aroclor	1016	1242	1248a	1248g	1254a	1254g	1260	1262a	1262g
fraction for 144 PCB congeners in Mix 1-5	0.9961	0.9935	0.9880	0.9904	0.9940	0.9929	0.9982	0.9966	0.9971

Table 2 contains a comparison of the GC conditions and resolution achieved on the 3 different columns for the same mixture of 144 compounds. Figure 1 contains examples of chromatograms for the Mix 1-5 on each of the columns.

TABLE 2:Selected Properties of Compared GC Columns[a]

Column	Length (m)	Inner Diameter (mm)	Film Thickness (µm)	Analysis Time[b] (min)	Resolution[b] (peaks)
J&W DB-5	60	0.25	0.25	165	105
J&W DB-XLB	60	0.25	0.25	110	120
SGE HT8-PCB	60	0.25	X*	61	117

[a] Using GC Methods Described in Materials and Methods

[b] For 144 PCB Congener Mixture (144 Possible Peaks).

It can be seen that the installation of the HT8-PCB column, while decreasing the overall resolution by 3 peaks (ca. 3%), improved the analysis time by 49 minutes, resulting in an analysis time of 61 minutes for the 144 congener mix. Preliminary work

Figure 2, shown below, illustrates the chromatographic comparison of the nine Aroclor mixtures on the 60 m HT8-PCB column. The congener composition of the most common Aroclor mixtures (1242, 1254, and 1260) are in good agreement with previously published results as determined by congener plots, Principal Component Analysis and Cosine Theta similarity matrix (described elsewhere)[8]. Table 3 contains the congener composition of Aroclor 1268 which is the first published congener composition we are aware of for this Aroclor although others have presented chromatogram for this Aroclor[9]. Since our other Aroclor compositions were so close to those published we are confident in the results but intend to carry out additional confirmation by GC-MS and/or second column analysis. The concentration of Aroclor mixtures, as Aroclor equivalents and that determined from congener specific analysis (details available elsewhere[5])

60 m HT8-PCB

60 m DB-5 IADN Program

60 m DB-XLB Program 1

60 m DB-XLB Program 2

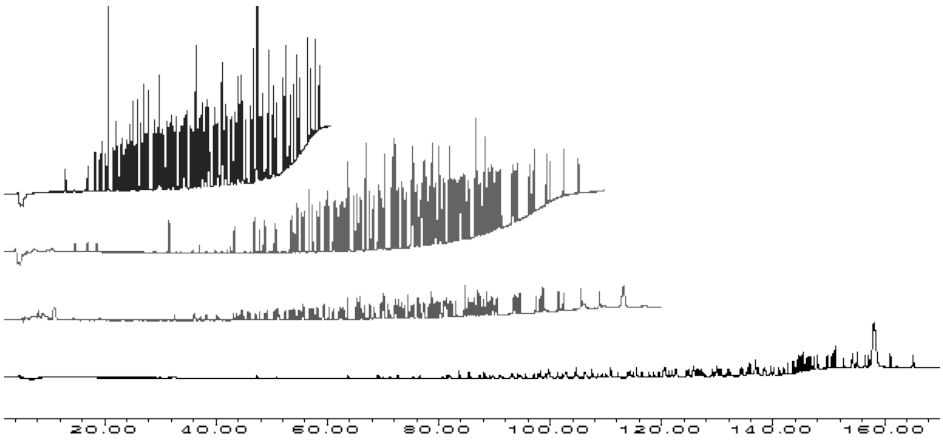

Figure 1. Chromatographic comparison of 10 pg/uL AccuStandard Mixes 1-5 (144 PCB congeners) on 3 different GC capillary columns (conditions as per Materials and Methods)

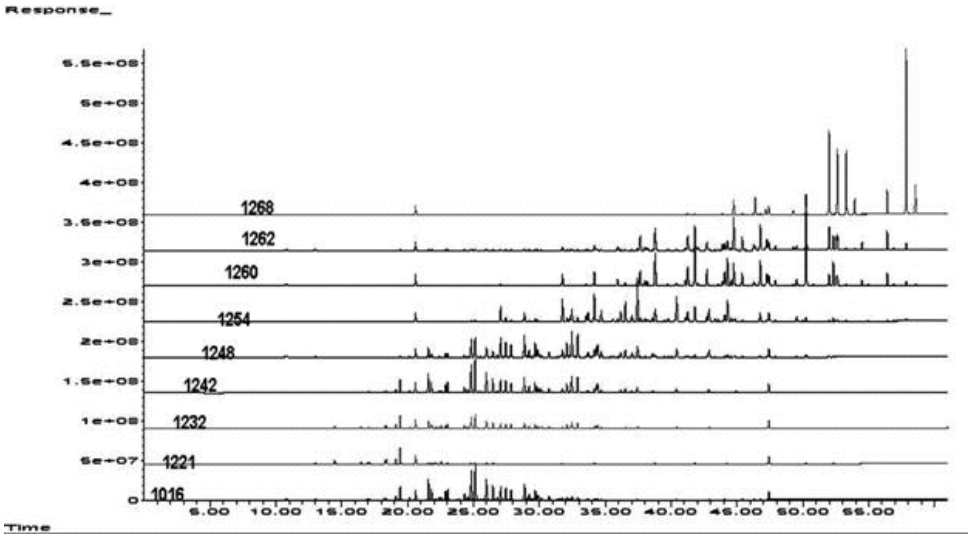

Figure 2. Chromatographic comparison of nine different Aroclor mixtures using HT8-PCB column

Table 3: Congener Composition for Aroclor 1268

IUPAC	**128, 174**	**132, 179**	**170**	**178**	**180**	**183**	**187**	**194**	**195**	**197**	**199**	**200**	**206**	**207**	**208**	**209**
Relative Weight																
Fraction	0.0008	0.0007	0.0007	0.0006	0.0151	0.0019	0.0424	0.0463	0.0013	0.0002	0.1954	0.0105	0.3926	0.0347	0.1590	0.0978

provided concentrations within 10% of each other. This indicates that congener specific analysis can also provide “Aroclor equivalent” results, where the congener composition is similar enough to one (or more) Aroclors.

Future work is expected to involve i)identifying appropriate fluorinated-PCBs for replacing the “non-Aroclor” congeners presently being used ii) studies on accuracy and precision from increasing number of points for the calibration curves iii) analysis for additional mixtures for up to 209 congeners and iv). analysis of PCBs in environmental and clinical samples

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