

# MULTIDIMENSIONAL GAS CHROMATOGRAPHY - MASS SPECTROMETRY AS A METHOD FOR THE DETERMINATION OF COPLANAR PCB CONGENERS

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**ABSTRACT:** Multidimensional gas chromatography - mass spectrometry (GC/GC/MS) was applied for the determination of some toxic PCB congeners in three Aroclor mixtures. The results are mainly in accordance with earlier studies except for 3,3',4,4',5,5'-hexachlorobiphenyl (IUPAC no. 169) which was not observed in any of the investigated materials.

## INTRODUCTION

The toxicity of polychlorinated biphenyls (PCB) is mostly due to non-*ortho*- and mono-*ortho*-chlorine substituted congeners. Their relative potencies of induction for aryl hydrocarbon hydroxylase (AHH) and *ethoxy resorufin O-deethylase* (EROD) responses are close to those of chlorinated dibenzodioxins and furans (PCDD/F) (1). There are reports which indicate that the toxic burden caused by these PCB congeners into the environment is several orders of magnitude higher than that of PCDD/F because of the higher concentration levels (2-4). Therefore the toxicological importance of the samples can be estimated only after concentrations of the most active congeners are known.

The analysis of toxic PCB congeners in biological matrices makes strict demands on the methods used. Two principal types of procedures have been reported: an activated charcoal chromatography based sample purification (5) and utilization of multidimensional gas chromatography (GC/GC) (6, 7).

Duinker et al. employed GC/GC with electron capture detectors for the separation of toxic coplanar PCB congeners (6) and even for the complete characterization of commercial mixtures (7). Schomburg and co-workers (8) had earlier applied GC/GC for the separation of PCB, PCDD and PCDF congeners. Ligon and May (9) used a GC/GC instrument coupled with a mass spectrometer for the determination of some environmental target compounds.

We have applied multidimensional gas chromatography - mass spectrometry (GC/GC/MS), according to our knowledge for the first time, for the determination of non-ortho- and mono-orthochlorine substituted PCB congeners. In this work we demonstrate the applicability of the technique by describing the analysis of some of these compounds in Aroclor mixtures.

## MATERIALS AND METHODS

Standard Aroclor mixtures and single congeners: The Aroclor mixtures 1242, 1254 and 1260 were obtained from AccuStandard Inc., New Haven, CT, USA. The single congeners were from AccuStandard and Cambridge Isotope Laboratories (CIL), Woburn, Mass., USA. <sup>13</sup>C-labelled 3,3',4,4',5-pentachlorobiphenyl (IUPAC no. 126) used as the internal standard was also from CIL. Iso-octane (HPLC grade) was from Rathburn Chemicals Ltd., Walkersburn, Scotland.

The instrumental system: For the details of the system see Table 1.

Table 1. Technical details of instrumental system.

Gas chromatograph:	Varian 3400
GC temperature program:	100°C (1 min), (50°C/min) -> 160°C, (5°C/min) -> 200°C, (50°C/min) -> 240°C (35min)
Injector:	Varian temperature programmable on-column injector
Injector temperature program:	100°C (1min) -> 300°C (300°C/min)
GC/GC device:	SGE (Scientific Glass Engineering Inc.) Column Switching System
First (pre-) column:	10 m, 0.32 mm i.d., 0.25 µm CP-Sil 8CB (Chrompack, Middelburg, Netherlands)
Second (analytical) column:	30 m, 0.25 mm i.d., 0.25 µm DB-FFAP (J&W Scientific, Folsom, California, USA)
Monitor detector:	Varian electron capture detector
Main detector:	Finnigan Incos 50 quadrupole mass spectrometer, EI-mode
Ions monitored:	- IUPAC nos. 77 and 81: 292 amu - IUPAC nos. 105 and 126: 326 amu - IUPAC no. <sup>13</sup> C-126: 338 amu - IUPAC no. 169: 358-362 amu (scanned)

All the fractions transferred from the first column were collected into a cold trap situated at the inlet of the second column and eluted after trapping to the MS. Elution in the first column was carried out by using fast temperature programming in order to shorten the run time (Table 1.) while isothermal conditions were used for the second separation process. The scanning program of MS was designed to monitor only the M<sup>+</sup> ion of each isomer group at a time except for congener no. 169 which was measured by scanning from 358 to 362 amu in order to optimize sensitivity.

The widths of the fractions heartcutted were between 20 and 40 seconds. Rather wide windows had to be employed because dead volume in the SGE column switching system caused some peak broadening.

The Varian 3400 GC's built-in external relay control system was employed for correct timing of the heart-cut window relative to the temperature program of the GC.

Identification of the PCB congeners was performed on the basis of relative retention times (RRT) and the monitoring of M<sup>+</sup> ions of the congeners. RRTs and response factors (RRF) were calculated relative to <sup>13</sup>C-labelled congener no. 126 which was also used as the quantitative internal standard. The detection limits, calculated as peaks with a height of ten times noise, were 10 pg for IUPAC no. 77, 7 pg for no. 81, 20 pg for nos 105 and 126 and 70 pg for no. 169.

## RESULTS AND DISCUSSION

RRT and RRF values are listed in Table 2 and the results in Table 3.

Table 2. Relative retention times (RRTs) and response factors (RRFs) of coplanar PCB congeners. RRTs and RRFs were calculated as a mean of six runs of standard solution. Both RRTs and RRFs are calculated against <sup>13</sup>C-labelled congener IUPAC no. 126. S.D. stands for standard deviation (%).

	Congener (IUPAC no.)				
	77	81	105	126	169
RRT	0.8335	0.7922	0.9000	1.001	1.268
S.D. %	0.38	0.24	0.13	0.32	0.19
RRF	2.09	3.12	1.90	2.22	1.60
S.D. %	23	23	17	21	15

Possible coelution of congeners with another chlorination degree was checked by running the samples monitoring all relevant molecular ions of PCB congeners. Coelution of congener IUPAC no. 81 with some penta- and hexachlorinated congeners - yet unidentified - was observed.

At this stage possible coelution of congeners with same chlorination degree was checked by using data from earlier studies. Congeners which elute close enough with the analyzed ones from the SE-54 column to be heartcutted were searched using the data from Mullin et al. (10). It should be noted that the coplanar congeners 77, 126 and 169 typically elute as the last peaks of each isomeric group. Because of this fact isomeric coelution does not seem to happen. It will be a subject for further studies to use individual congeners for confirmation.

Table 3. Percent contribution of some toxic PCB congeners in Aroclor mixtures.

	Congener (IUPAC no.)			
	77	105	126	169
Aroclor 1242:				
- this work	0.22	0.29	0.003	<0.007
- ref. 6	0.50	0.33	<0.01	<0.01
- ref. 7	0.45	0.86	<0.05	<0.05
Aroclor 1254:				
- this work	0.25	6.9	0.016	<0.007
- ref. 6	<0.01	2.03	<0.01	0.08
- ref. 7	<0.05	3.83	<0.05	<0.05
Aroclor 1260:				
- this work	0.017	0.052	<0.002	<0.007
- ref. 6	<0.01	0.08	<0.01	0.05
- ref. 7	<0.05	0.07	<0.05	0.05

Our results are mainly in good accordance with earlier reports obtained by GC/GC/ECD technique. To some extent the minor differences might be due to batch to batch variations in the composition of commercial mixtures. The most striking difference is in the concentrations of congener no. 169 which we did not observe in any of the investigated materials despite of adequate sensitivity and high selectivity of detection.

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