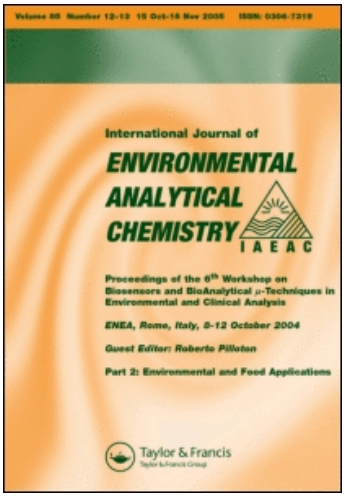

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COMPOSITION OF PCB ISOMERS AND CONGENERS IN TECHNICAL CHLOROFEN FORMULATION PRODUCED IN POLAND

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The composition of Chlorofen, a technical formulation of polychlorinated biphenyls (PCBs) produced in Poland, has been investigated using GC-ECD and GC-MS techniques. Chlorofen was a highly chlorinated mixture (63.6% Cl), mainly composed of PCB members with 5 to 9 chlorine atoms which comprised 99.55% of total PCBs. The average number of Cl per molecule in Chlorofen was 7.3, and the average molecular weight was 405.4. It was found that Chlorofen contained at least 59 PCB congeners with the major components such as IUPAC No. 153 of hexa-, 176, 180, 187 of hepta-, 194, 195, 198, 201/196 of octa- and 206 of nonachlorobiphenyls. Additionally, three components of highly toxic non-*ortho* chlorine substituted coplanar PCBs (IUPAC Nos 77, 126 and 169) were also quantified at a concentration of 0.52, 0.25 and 0.43 $\mu g\ g^{-1}$, respectively, the latter (169), showing a greater content than in Aroclor and Kanechlor formulations.

KEY WORDS: Chlorofen, PCBs, coplanar PCBs, isomer-specific analysis, Poland.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are inert compounds with high thermal stability, chemical resistance and excellent dielectric properties. Because of these acceptable physical and chemical properties, PCB preparations have been used for diverse technical appliances, particularly as dielectric fluids in industrial operations, heat transfer applications and plasticizers.[1] There exists a wide range of technical PCB formulations under different trade names such as Aroclor (United States) Clophen (Germany), Kanechlor (Japan), Phenoclor and Pyralene (France), Fenoclor (Italy) etc. Efforts have been undertaken to elucidate the complex composition of most of the above cited technical PCB mixtures which are the world's major formulations.[2–6]

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On the other hand, less information is available about minor producers of PCBs and their characteristics.

As one of the minor producers, Poland has a single formulation of technical PCBs dealing with the trade name as Chlorofen.[7] This formulation is a light-brown sticky and viscous resin. No data is available about the quantum of production, manufacture time and usage of Chlorofen as well as its physical and chemical properties. An unauthorized source indicated that Chlorofen was used as a lubricant in hydraulic systems in coal mining equipment. According to the producer of Chlorofen, its major component was noted as pentachlorobiphenyl and the chlorine content was 59%.[7] The major objective of the present study is to determine PCB isomer and congener composition in technical Chlorofen using GC-ECD and GC-MS analysis. At the same time, this approach was also applied for the clarification of coplanar PCB contents in technical Chlorofen. Coplanar PCBs are highly toxic members posing great concern and toxic threat to humans and wildlife.[8–10]

MATERIALS AND METHODS

Chlorofen formulation used in this study originated from the laboratory of Państwowy Zakład Higieny in Warsaw.[7] Kanechlor 600 and the equivalent mixture of Kanechlor preparations (KC-300, KC-400, KC-500 and KC-600) were from Kanegafuchi Co. Ltd., Japan. Decachlorobiphenyl standard (99% purity) was a gift from Osaka Prefectural Laboratory of Public Health, Japan. Non-*ortho* coplanar PCB standards such as 3,3',4,4'-tetrachlorobiphenyl (IUPAC No. 77), 3,3',4,4',5-pentachlorobiphenyl (IUPAC No. 126) and 3,3',4,4',5,5'-hexachlorobiphenyl (IUPAC No. 169) were of 98–100% purity.[11]

Chlorofen formulation was prepared with hexane and its diluted solution was employed for GC-MS and GC-ECD quantification. Polychlorinated biphenyls excluding non-*ortho* coplanar members (IUPAC Nos. 77, 126 and 169) in Chlorofen formulation were determined using the equivalent mixture of Kanechlor preparations as a standard, where contents of individual isomers and congeners were already known.[6] Decachlorobiphenyl in Chlorofen was measured using an authentic standard of this isomer. The non-*ortho* coplanar PCBs were determined using carbon column chromatography. Activated carbon of the following particle size composition was purchased from Wako Pure Chemical Co. Ltd., Japan: coarser (297 μ) < 40%; 297–63 μ < 50%; finer than 63 μ < 10%.

The analytical procedure used for separation of three non-*ortho* coplanar PCBs was the same as that of our previous report.[11]

A gas chromatograph (Hewlett Packard 5890 Series II) equipped with moving needle type injection port and ^{63}Ni electron capture detector (ECD) was employed for the determination of PCB isomers and congeners including decachlorobiphenyl. A fused silica capillary column (30 m × 0.25 mm i.d.), coated with chemically bonded DB-1 (100% dimethyl polysiloxane), having a film thickness of 0.25 μm (J & W Scientific, Folsom, CA, USA) was used. The operating conditions of the GC column oven were as follows: initial temperature 160°C, initial time 10 min, rate 2°C min^{-1},

final temperature 250°C and final time 15 min. Injector and detector temperatures were maintained at 300°C. Helium was used as carrier gas at a flow rate of 1.04 kg cm^{-2}, whereas nitrogen at 1.40 kg cm^{-2} was used as make up gas.

A gas chromatograph-mass spectrometer system (Hewlett Packard 5890 GC with 5970 Mass selective detector) in the electron impact mode (70 eV) was also used for the determination and identification of PCB isomers and congeners. A fused silica capillary column (30 m × 0.25 mm i.d.), coated with chemically bonded DB-1701 (14% cyanopropylphenyl and 86% dimethyl polysiloxane), with film thickness of 0.25 μm was employed for analysis of non-*ortho* chlorine substituted coplanar PCBs and an analogue column with DB-1 for the other PCB congeners. The operating conditions were as follows: injection port temperature 260°C and transfer line 280°C, initial column temperature for analysis of coplanar PCBs 180°C, rate 2°C min^{-1}, final temperature 250°C, final time 35 min. Column initial temperature for other PCBs 140°C, rate 2.5°C min^{-1}, final temperature 250°C and final time 10 min.

A Hewlett-Packard 59970C data system was used to aid in the quantification of PCB isomers and congeners. For the confirmation/quantification of three non-*ortho* coplanar PCBs, M^+ and $(M + 2)^+$ ions were monitored at *m/z* 290 and 292 for IUPAC No. 77, *m/z* 324 an 326 for IUPAC No. 126, and *m/z* 358 and 360 for IUPAC No. 169 and the intensity ratio of these ions was compared with that of the standard. The other PCB isomers and congeners were quantified by selective ion monitoring (SIM) at *m/z* 222, 256, 292, 326, 360, 394, 428 and 464 for di, tri-, tetra-, penta-, hexa-, hepta-, octa-, and nonachlorobiphenyls, respectively.

Table 1 Comparison of PCB compositions in Chlorofen, Kanechlor 600, Clophen A60 and Aroclor 1260

Composition (%)	*Chlorofen*	*Kanechlor 600*	*Clophen A60**	*Aroclor 1260**
Monochlorobiphenyls	0	0	0	0
Di-	0	0.10	0	0
Tri-	0.02	0.79	0	0.08
Tetra-	0.03	1.30	0.60	0.77
Penta-	0.22	8.42	14.35	11.82
Hexa-	12.16	34.82	48.84	44.59
Hepta-	49.19	47.74	29.25	34.20
Octa-	31.80	11.15	6.39	7.73
Nona-	6.40	0.68	0.57	0.74
Deca-	0.18	0	0.05	0.07
Chlorine contents %	63.6	60.7	59.6	60.1
Average number of Cl per molecule	7.3	6.5	6.2	6.3
Average molecular weight	405.4	376.8	369.0	372.8

* Data on Clophen A60 and Aroclor 1260 were calculated from Ref. [5].

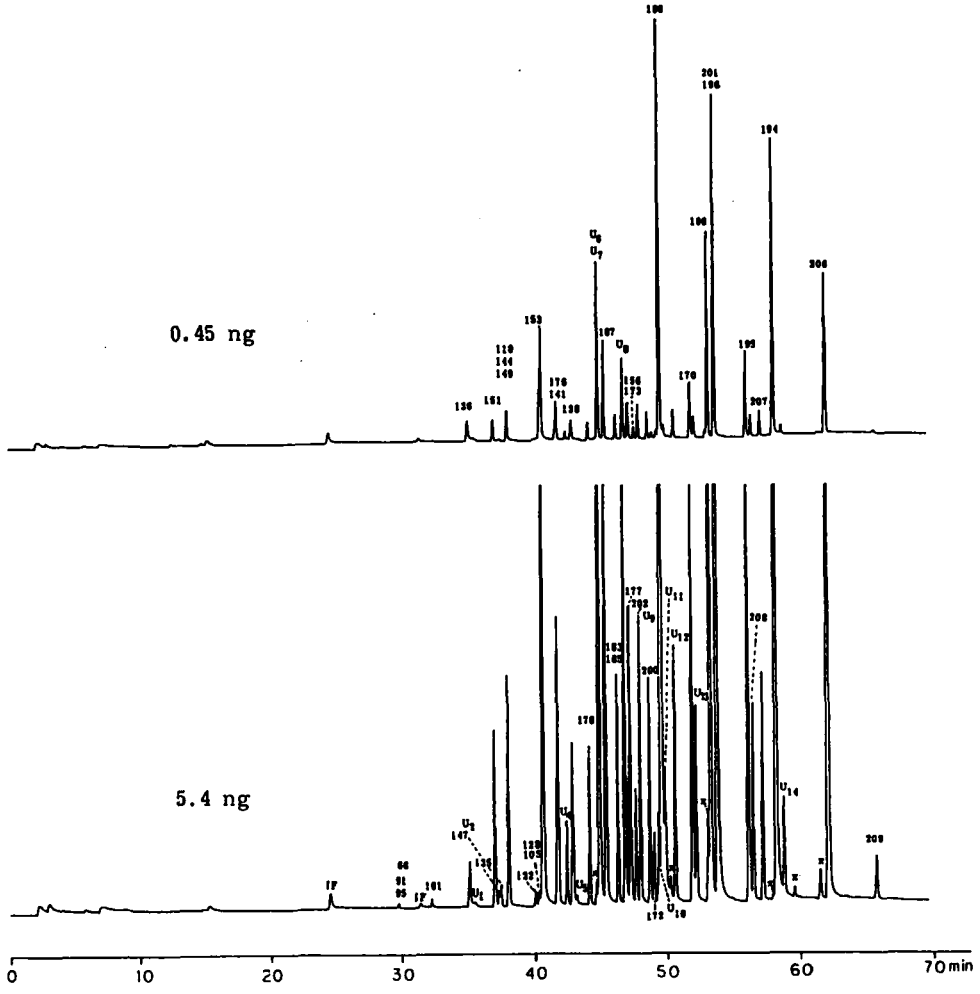

Figure 1 Gas chromatogram of Chlorofen formulation. The detailed condition of gas chromatography are given in the text. Peak numbers are based upon the IUPAC numbering system, Ref. [2]. U-peak shows chlorobiphenyls of unknown structure; x-peak reveals the unknown chemicals other than PCBs.

RESULTS AND DISCUSSION

The isomer-specific analysis of PCBs using GC-ECD and GC-MS revealed that the commercial Chlorofen formulation was mainly composed of hepta- (49.19%), octa- (31.88%), hexa- (12.16%) and nonachlorobiphenyls (6.40%) (Table 1). Such a Chlorofen composition is disagreed with that "described by producer", as to be pentachlorobiphenyl.[7] The PCB composition of Chlorofen is quite different when compared with highly chlorinated PCB formulations like Kanechlor KC 600, Clophen A60 and Aroclor 1260. Chlorofen contained larger proportion of nona- and

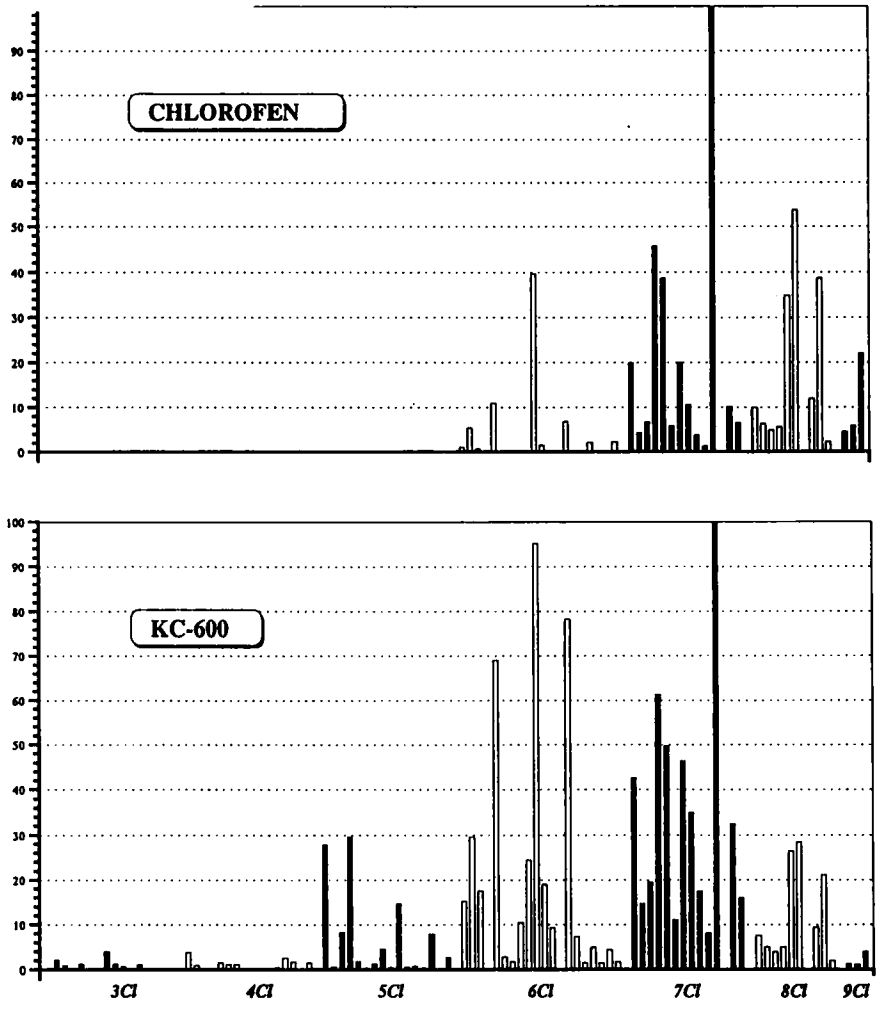

Figure 2 Schematic composition of PCB isomers and congeners in Chlorofen and Kanechlor 600 formulations. Content of the highest peak (IUPAC No. 180) was treated as 100. For details of PCB congeners and their structures, see Ref. [6].

octachlorobiphenyls and less of penta- and hexachlorobiphenyls than the referred formulations (Table 1). The average number of chlorine per biphenyl molecule, the average molecular weight and chlorine content were higher in Chlorofen than in Kanechlor 600, Clophen A60, and Aroclor 1260 formulations. The chlorine content of Chlorofen is comparable with the chlorine content of Aroclor 1262—which seemed to have similar appearance to Chlorofen like viscous sticky resin with light yellow colour.[1]

It was possible to separate Chlorofen formulation into 40 peaks of chlorobiphenyls using capillary column gas chromatography (Figure 1). Even using the present

Table 2 Composition of Chlorobiphenyls in Chlorofen formulation

IUPAC numbering	*Structure*	*Content (%)*	*IUPAC numbering*	*Structure*	*Content (%)*
28	2,4,4′	0.01	U_4	hepta-CB	0.76
31	2,4′,5		138	2,2′,3,4,4′,5	1.18
20	2,3,3′	<0.01	U_5	hexa-CB	0.05
52	2,2′,5,5′	<0.01	178	2,2′,3,3′,5,5′,6	1.17
37	3,4,4′	0.01	U_6	hepta-CB	7.87
41	2,2′,3,4	<0.01	U_7	hexa-CB	0.39
64	2,3,4′,6		187	2,2′,3,4′,5,5′,6	6.66
58	2,3,3′,5	<0.01	185	2,2′,3,4,5,5′,6	1.01
74	2,4,4′,5		183	2,2′,3,4,4′,5′6	
70	2,3′,4′,5	0.01	U_8	hepta-CB	3.43
66	2,3′,4,4′	0.01	177	2,2′,3,3′,4′,5,6	1.85
91	2,2′,3,4′,6	0.04	173	2,2′,3,3′,4,5,6	0.67
95	2,2′,3,5′,6		156	2,3,3′,4,4′,5	0.04
60	2,3,4,4′	0.01	202	2,2′,3,3′,5,5′,6,6′	1.72
101	2,2′,4,5,5′	0.05	U_9	hexa-CB	0.40
97	2,2′,3′,4,5	<0.01	200	2,2′,3,3′,4,5′,6,6′	1.12
113	2,3,3′,5′,6		172	2,2′,3,3′,4′,5,5′	0.25
87	2,2′,3,4,5	0.01	U_{10}	octa-CB	0.86
117	2,3,4′,5,6		180	2,2′,3,4,4′,5,5′	17.21
85	2,2′,3,4,4′	<0.01	U_{11}	hepta-CB	<0.01
136	2,2′,3,3′,6,6′	0.20	U_{12}	octa-CB	0.97
U_1	penta-CB	0.02	170	2,2′,3,3′,4,4′,5	1.77
151	2,2′,3,5,5′,6	0.95	U_{13}	hepta-CB	1.15
135	2,2′,3,3′,5,6	0.14	198	2,2′,3,3′,4,5,5′,6	6.00
147	2,2′,3,4′,5,6		201	2,2′3,3′,4′,5,5′,6	9.26
U_2	penta-CB	<0.01	196	2,2′,3,3′,4,4′,5′,6	
U_3	penta-CB	<0.01	195	2,2′,3,3′,4,4′,5,6	2.06
118	2,3′,4,4′,5	0.09	208	2,2′,3,3′,4,5,5′,6,6′	0.78
144	2,2′3,4,5′,6	1.89	207	2,2′,3,3′,4,4′,5,6,6′	1.05
149	2,2′,3,4′,5′,6		194	2,2′,3,3′,4,4′,5,5′	6.64
132	2,2′,3,3′,4,6	0.05	U_{14}	octa-CB	0.41
128	2,2′,3,3′,4,4′	0.06	206	2,2′,3,3′,4,4′,5,5′,6	3.79
105	2,3,3′,4,4′	0.01	209	2,2′,3,3′,4,4′,5,5′,6,6′	0.16
153	2,2′4,4′,5,5′	6.82			
176	2,2′,3,3′,4,6,6′	3.43			
141	2,2′,3,4,5,5′	0.26			

U: chlorobiphenyls for which no standards were available.
CB: chlorobiphenyl.

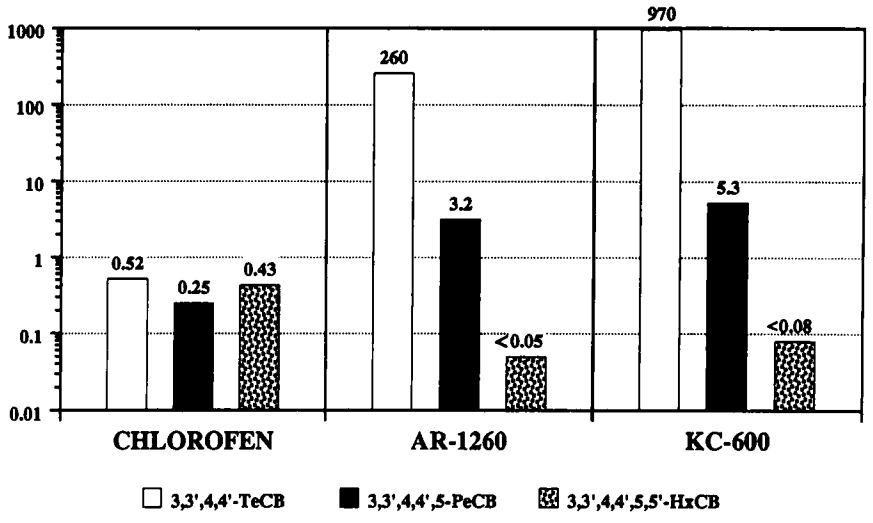

Figure 3 Compositions of three non-*ortho* coplanar PCB congeners in Chlorofen, Aroclor 1260 and Kanechlor 600 formulations. Data for the later two technical mixtures were cited from Ref. [12]. The figures on the bars indicate the concentrations (ng g^{-1}) of individual non-*ortho* coplanar PCB in total PCBs.

analytical procedure and quantification systems, most of tri-, tetra- and penta-chlorobiphenyls could not be traced on the chromatogram, indicating extremely low concentrations of these less chlorinated members. During a course of GC-MS analysis, 59 peaks of PCBs were observed on the mass fragmentogram. Schematic representation of chlorobiphenyl compositions in Chlorofen as well as Kanechlor 600 are given in Figure 2, indicating again the highly chlorinated pattern in the Polish PCB product. Among the 59 peaks identified by GC-MS, Chlorofen was found to contain 24 PCB peaks at composition below 0.1% and 21 peaks more than 1.0%, while still 14 peaks were of unknown structures (three penta-, three hexa-, five hepta- and three octachlorobiphenyls) (Table 2). The congeners such as 2,2',3,4,4',5,5'-heptachlorobiphenyl (IUPAC No. 180), 2,2',3,3',4',5,5',6-/2,2',3,3',4,4',5',6- octachlorobiphenyls (IUPAC Nos 201/196), U_6-heptachlorobiphenyl, 2,2',4,4',5,5'-hexachlorobiphenyl (IUPAC No. 153), 2,2',3,4',5,5',6-heptachlorobiphenyl (IUPAC No. 187), 2,2',3,3',4,4',5,5'-octachlorobiphenyl (IUPAC No. 194), 2,2',3,3',4,5,5',6-octachlorobiphenyl (IUPAC No. 198), 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl (IUPAC No. 206), 2,2',3,3',4,6,6'-heptachlorobiphenyl (IUPAC No. 176, U_8-heptachlorobiphenyl, and 2,2',3,3',4,4',5,6-octachlorobiphenyl (IUPAC No. 195) were found to be major components in Chlorofen. Their percentage compositions in this formulation was 17.21, 9.26, 7.87, 6.82, 6.66, 6.64, 6.00, 3.79, 3.43, 3.43 and 2.06, respectively. These PCB members represented about 70% of the total PCBs.

Besides *ortho*-chlorine substituted congeners of PCBs, non-*ortho* coplanar members (IUPAC Nos 77, 126 and 169) were also identified and quantified in Chlorofen formulation (Figure 3). These three non-*ortho* coplanar PCBs are known as highly

toxic and usually present at low concentrations in commercial PCB formulations.[12] The concentrations of highly toxic coplanar 3,3',4,4'-tetrachlorobiphenyl (IUPAC No. 77) and 3,3',4,4',5-pentachlorobiphenyl (IUPAC No. 126) in Chlorofen were found to be 0.52 and 0.25 $\mu g\ g^{-1}$ respectively, which were much lower than in Aroclor 1260 and Kanechlor 600. On the other hand, 3,3',4,4',5,5'-hexachlorobiphenyl (IUPAC No. 169) revealed a higher level in Chlorofen than in Kanechlor 600 and Aroclor 1260.

It has yet to be cleared whether Chlorofen or other imported products are major PCB formulations used in Poland. The monitoring survey for PCB contamination in various environmental samples using the isomer-specific technique may serve us an answer to this point. The present study provides a useful information in considering the source of PCBs contamination in the Polish environment as well as its toxic implication to humans and wildlife.

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